

Cu{001}c(2×2)-Pd: An ordered surface alloy

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A quantitative low-energy electron diffraction (LEED) intensity analysis shows that the room-temperature reaction of Pd atoms with a Cu{001} surface produces a surface alloy, Cu{100}c(2×2)-Pd, analogous to Cu{001}c(2×2)-Au. The structure of Cu{001}c(2×2)-Pd is almost planar, with the Pd atoms located 0.02 ± 0.03 Å outwards from the Cu atoms, and an interlayer distance from the Cu atoms to second (100% Cu) layer equal to the Cu{001} bulk interlayer spacing (1.807 Å). Although there are no ordered Pd atoms beyond the surface mixed layer, there is some evidence for disordered Pd either above or below the alloy layer. Angle-resolved photoemission spectra show that the valence band of the surface alloy is characterized by a well-defined Cu 3*d*-derived band and by the appearance of features due to Pd. The dispersion and the photon-energy dependence of these features suggest their probable origins and are consistent with the alloy character of Cu{001}c(2×2)-Pd.

I. INTRODUCTION

An ordered surface alloy is distinguished from an ordered bulk alloy by the fact that it is limited to a single ordered (usually a mixed) layer in the top atomic plane of a substrate with no penetration into the bulk of the substrate. The room-temperature reaction of Au atoms with a clean Cu{001} surface leads to the formation of such a surface alloy, denoted Cu{001}c(2×2)-Au, as demonstrated by both experimental¹ and theoretical² studies. Similar interactions between Au and Cu atoms have been predicted for other Cu surfaces, namely, Cu{111} and Cu{110} (Ref. 2), but not yet confirmed experimentally. A second example of surface-alloy formation is presented here: The reaction of Pd atoms with a clean Cu{001} surface leading to a Cu{001}c(2×2)-Pd phase. A brief report of the experimental work identifying this phase as a surface alloy was published earlier.³ We present here details of low-energy electron diffraction (LEED) experiments and of a quantitative LEED intensity analysis that determine the ordered atomic structure of the surface phase, and details of ultraviolet-photoemission-spectroscopy (UPS) experiments that confirm the alloy character of this phase in accordance with the LEED results.

Section II describes the experiments, Sec. III the LEED analysis and its results, Sec. IV the UPS observations and their interpretations, and Sec. V the overall conclusions.

II. EXPERIMENTS

The LEED and the UPS experiments were done in different chambers at different times, the UPS after the LEED analysis was completed. Characterization of the

surface structure after each preparation was done by means of LEED pattern geometry and LEED *I-V* spectra, thereby insuring that the same structure was being studied in each experiment.

Sample preparation consisted of *in situ* cleaning of a Cu{001} surface (argon ion bombardments, 5×10^{-5} Torr, 500 eV, 8 μA for 20 min, followed by 600°C anneals for 10 min) and subsequent deposition of Pd on the unheated Cu{001} substrate. The Pd source was a Pd ribbon wrapped in Ta foil and heated electrically to about 1000°C. Auger-electron spectroscopy (AES) confirmed the absence of O, C, and S impurities from the surfaces studied, and helped determine the rate of deposition of Pd through the growth in intensity of the (doubly differentiated) Pd AES line at 330 eV. Figure 1 depicts such growth as a function of deposition time: the relationship seems to be linear but with two changes of slope. Such changes of slope, in this kind of plot, are usually interpreted as signaling the completion of full monolayers of deposited atoms. The LEED patterns, as annotated in Fig. 1, revealed the formation of a c(2×2) structure, with the "best" LEED pattern, in terms of sharpness and contrast, being observed in the vicinity of the first change in slope. Thus, the most immediate conclusion from these observations is that the best c(2×2) structure is formed at a surface coverage close to one monolayer, a conclusion that was reached both by Graham⁴ and by us in the earlier report of this work.³ However, this assumption is difficult to reconcile with the knowledge acquired from the LEED analysis (discussed below), namely, that the c(2×2) structure is an ordered mixed layer of Pd and Cu atoms. It therefore seems more plausible to interpret the first change of slope in the plot of Fig. 1 as the completion of the c(2×2) mixed layer, which ideally requires a coverage of only $\frac{1}{2}$ monolayer equivalent of Pd. The best c(2×2) pattern would then be expected at or near this coverage. Accordingly, the second change in

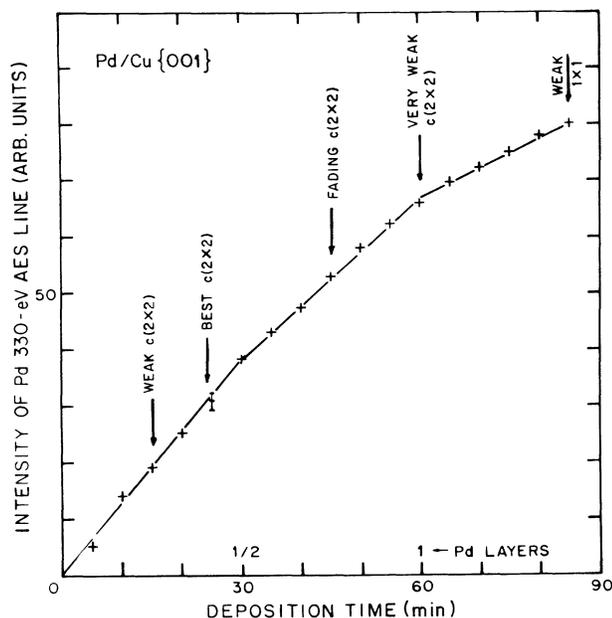


FIG. 1. Growth of the doubly differentiated AES line of Pd at 330 eV with increasing time of Pd deposition.

slope may be attributed to full coverage of the surface by at least an additional $\frac{1}{2}$ monolayer equivalent of Pd. The LEED observations indicate that this additional deposit was not ordered.

In general, the LEED patterns obtained after deposition of Pd had noticeably higher background than those from the clean Cu surface, especially at high incident-electron energies. This observation suggests that even when the best $c(2 \times 2)$ pattern was observed the surface was not fully ordered, i.e., that some fraction of the deposited Pd atoms was disordered, hence not in the $c(2 \times 2)$ structure.

The LEED intensity data were collected at room temperature with a LEED video analyzer involving a television camera and a microcomputer,⁵ the energy of the incident electrons varying from 40 to 300 eV. The following LEED spectra were recorded from the Cu{001} $c(2 \times 2)$ -Pd structure: at normal incidence ($\theta=0^\circ$), 10, 11, 20, $\frac{1}{2} \frac{1}{2}$, and $\frac{3}{2} \frac{1}{2}$; at $\theta=10^\circ$ and $\phi=0^\circ$, 00, 10, $0 \bar{1}$, $\frac{1}{2} \frac{1}{2}$, and $\frac{1}{2} \frac{3}{2}$. Several sets of data were collected independently from newly prepared surfaces, and two sets for each angle of incidence were selected for the structure analysis. The data were normalized to constant incident current and corrected for subtraction of the background.

The photoemission experiments were done at the National Synchrotron Light Source in a chamber hosting LEED and AES facilities, a Cu{001} sample and a Pd{001} sample, in addition to the Pd source. The light dispersing element was a plane-grating monochromator and the electron detector was a hemispherical analyzer (Vacuum Generator) with 2.4° acceptance angle and total resolution of about 0.3 eV as measured at the Fermi level of Au.

III. LEED

The calculations of LEED intensities were done with the CHANGE program.⁶ Both the Cu and the Pd potentials were taken from the compilation of Moruzzi, Janak, and Williams,⁷ and 8 phase shifts and 45 beams were used to represent the wave function. The inner potential was chosen initially as $V_0 = -(10 + 0.85E^{1/3}i)$ eV (with E in eV) and the real part was allowed to vary during the analysis in order to achieve the best fit to experiment. The root-mean square of atomic vibrations was chosen to be the same for all atoms involved, either on the surface or in the bulk, namely, $(\langle u^2 \rangle)^{1/2} = 0.15 \text{ \AA}$.

The structure analysis included two models of the $c(2 \times 2)$ structure: an overlayer of Pd with the Pd atoms located in the fourfold symmetrical hollows of the Cu{001} net, and a mixed layer with the Pd atoms replacing every other Cu atom in the top atomic plane of the substrate. In both models, some of the structural parameters were varied in the course of the analysis. In the overlayer model, the distance between the Pd (planar) overlayer and the top atomic plane of the Cu substrate was varied from 1.74 to 2.14 \AA in steps of 0.5 \AA (the "hard-sphere" interlayer distance is 1.94 \AA). In the mixed-layer model, the layer was assumed to be either planar or buckled, with the Pd atoms outwards of the Cu atoms by 0.05 or 0.1 \AA , and the first interlayer spacing (as measured from the Cu atoms in the mixed layer) was varied from 1.607 to 2.007 \AA in steps of 0.05 \AA (bulk value 1.807 \AA).

Evaluation of the fit to experiment was done both visually and by r -factor analysis.⁸ It appeared obvious in the early stages of the analysis that the overlayer model, even when optimized, did not fit the experimental data as well as the mixed-layer model. The refinement was therefore carried out only for the latter.

Minimization of the r factor was done for the mixed-layer model on a plane defined by the magnitude of the buckling versus the relaxation of the first interlayer spacing: the location of the minimum r factor gave the best values of these structural parameters. This minimization was done independently for four sets of data, two at normal incidence and two for the angles $\theta=10^\circ$ and $\phi=0^\circ$. The results were as follows. Buckling of the mixed layer (with Pd outwards): 0.020, 0.028, 0.030, and 0.009 \AA , respectively, for the four sets; first layer relaxation Δd_{12} (measured from the Cu atoms in the mixed layer), -0.016 , $+0.003$, $+0.005$, and 0.025 \AA , respectively. Average values and corresponding accuracies are then, for the buckling, $0.02 \pm 0.03 \text{ \AA}$ (Pd outwards), and for the interlayer spacing, $\Delta d_{12} = 0 \pm 0.03 \text{ \AA}$, with r -factor values of 0.11 and 0.21 for the $\theta=0^\circ$ and the $\theta=10^\circ, \phi=0^\circ$ data sets, respectively. The quality of the agreement between calculations and experiment can be checked in Fig. 2 for both angles of incidence involved.

The conclusion of the LEED analysis is thus as follows. The Cu{001} $c(2 \times 2)$ -Pd phase consists of a mixed layer of alternating Pd and Cu atoms on top of the Cu{001} substrate with no ordered Pd in the second layer. In our experiments some (undetermined) amount of disordered Pd atoms may have resided either above or

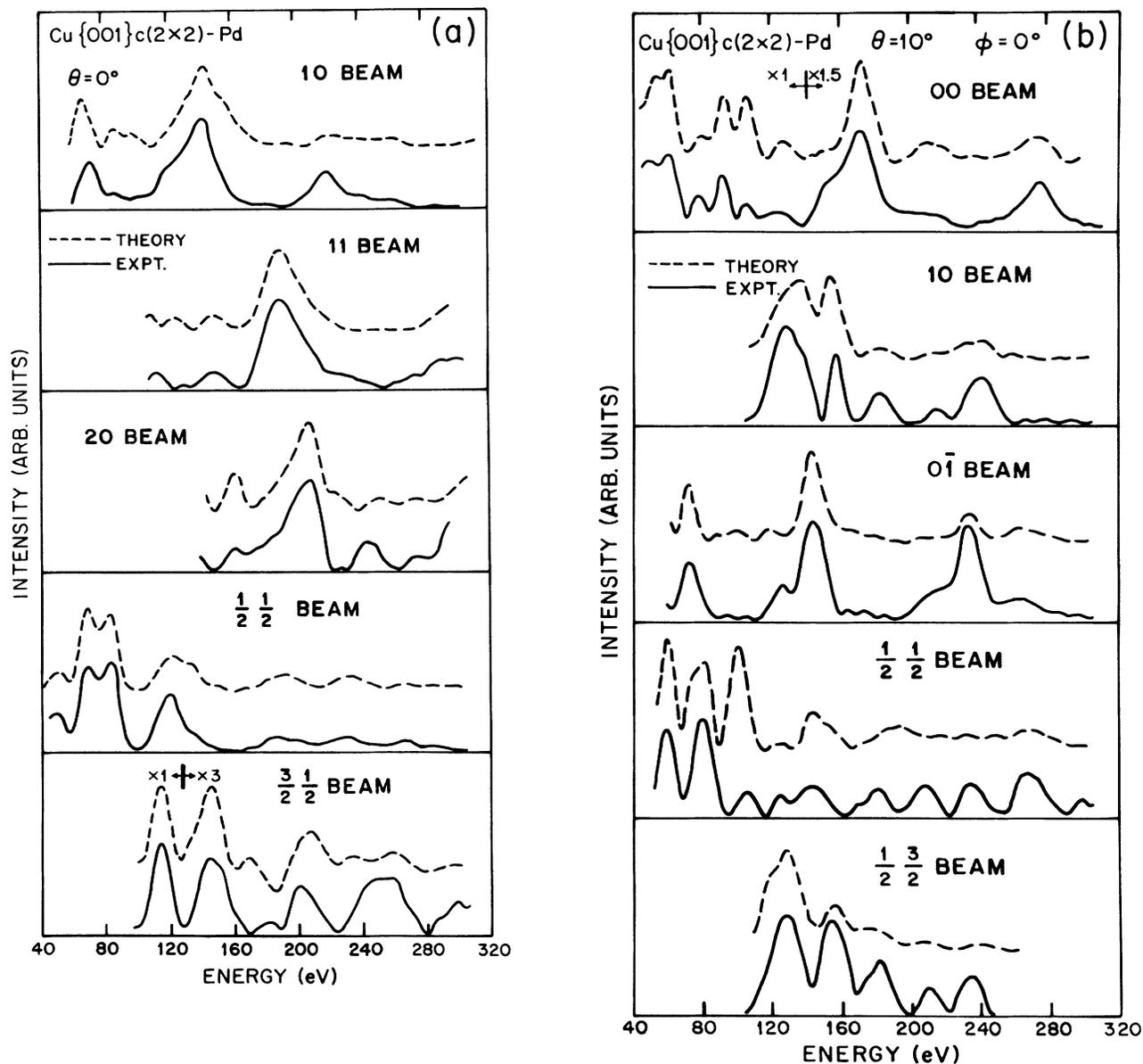


FIG. 2. (a) Normal incidence and (b) off-normal-incidence experimental and theoretical LEED spectra from the surface alloy Cu{001}c(2×2)-Pd.

below the mixed layer (as suggested by increased background of the $c(2 \times 2)$ pattern beyond that observed on the pattern from the clean Cu{001} surface). Addition of Pd to the $c(2 \times 2)$ phase does not produce growth of an ordered bulk phase, as evidenced by the fact that the LEED spectra do not change except for showing a decrease in overall intensity and increase of background. The Cu{001}c(2×2)-Pd phase is therefore a true surface alloy, similar to the Cu{001}c(2×2)-Au discussed elsewhere.¹ In contrast to the Cu-Au alloy, which exhibits a notable buckling, the Pd alloy is almost planar, with the Pd atoms only slightly displaced outwards of the Cu atoms. This difference is consistent with the 5% smaller size of the metallic radius of Pd compared to Au. In Table I we list the values of the Pd and Au radii in the

corresponding metals and alloys. Comparison between the structure of the Cu{001}c(2×2)-Pd surface alloy and that of the {001} surface of the Cu₃Pd bulk alloy is not possible because the latter structure is not known.

IV. PHOTOEMISSION

The experiments involved the collection of angle-resolved electron-distribution curves (EDC's) from clean Pd{001}, clean Cu{001}, and Cu{001}c(2×2)-Pd in various emission directions and for several photon energies ranging from 12.5 to 160 eV. The purpose of the experiments was to identify the changes caused by the alloy formation in the valence band of the Cu substrate, to compare the valence band of the Cu{001}c(2×2)-Pd sur-

TABLE I. Au and Pd radii compared in pure metals, bulk alloy, and surface alloy.

| | Radius (\AA) | Contraction (%) |
|--------------------|-------------------------|-----------------|
| Au | 1.442 | 0 |
| Cu ₃ Au | 1.380 | 4.3 |
| Cu{001}c(2×2)-Au | 1.280 ^a | 11.2 |
| Pd | 1.375 | 0 |
| Cu ₃ Pd | 1.340 ^b | 2.6 |
| Cu{001}c(2×2)-Pd | 1.278 ^c | 7.1 |

^aAllows for buckling of 0.1 \AA .

^bTheoretical value from the total-energy band theory for bulk crystal with a correction for thermal expansion [V. L. Moruzzi (unpublished)].

^cSame as the Cu bulk radius.

face alloy with that of a Pd{001} sample and, if possible, to test the consistency of the photoemission data with the atomic structure determined by the LEED analysis. The results, to be discussed in detail below, indicate that the incorporation of Pd in the Cu{001} surface gives rise to

three photoemission peaks, one at -0.7 eV, another at -1.7 eV, and a third at -4.8 eV (all binding energies are referred to the Fermi level taken as 0), and that the photon-energy dependence of these peaks is indeed consistent with the atomic structure determined with LEED. We present below the experimental evidence and some arguments for the probable origin of the observed peaks.

Figure 3 compares ECD's measured at normal emission from a clean Cu{001} surface on one hand and from a Cu{001}c(2×2)-Pd surface alloy on the other hand for photon energies varying between 13 and 130 eV. In addition to a small binding-energy shift of the major (Cu-derived) peak the curves reveal the appearance of three new features attributable to Pd. These are best seen in the EDC obtained with 60-eV photons: a small peak at -0.7 eV, a more pronounced peak at about -1.7 eV, and another peak at about -4.8 eV. The -0.7 -eV peak is not easily identifiable at lower photon energies, owing to the presence of notable Cu emission in the same binding-energy range, but is clearly seen at non-normal emission and will be discussed below. The other two peaks, at -1.7 and -4.8 eV, have also been observed by

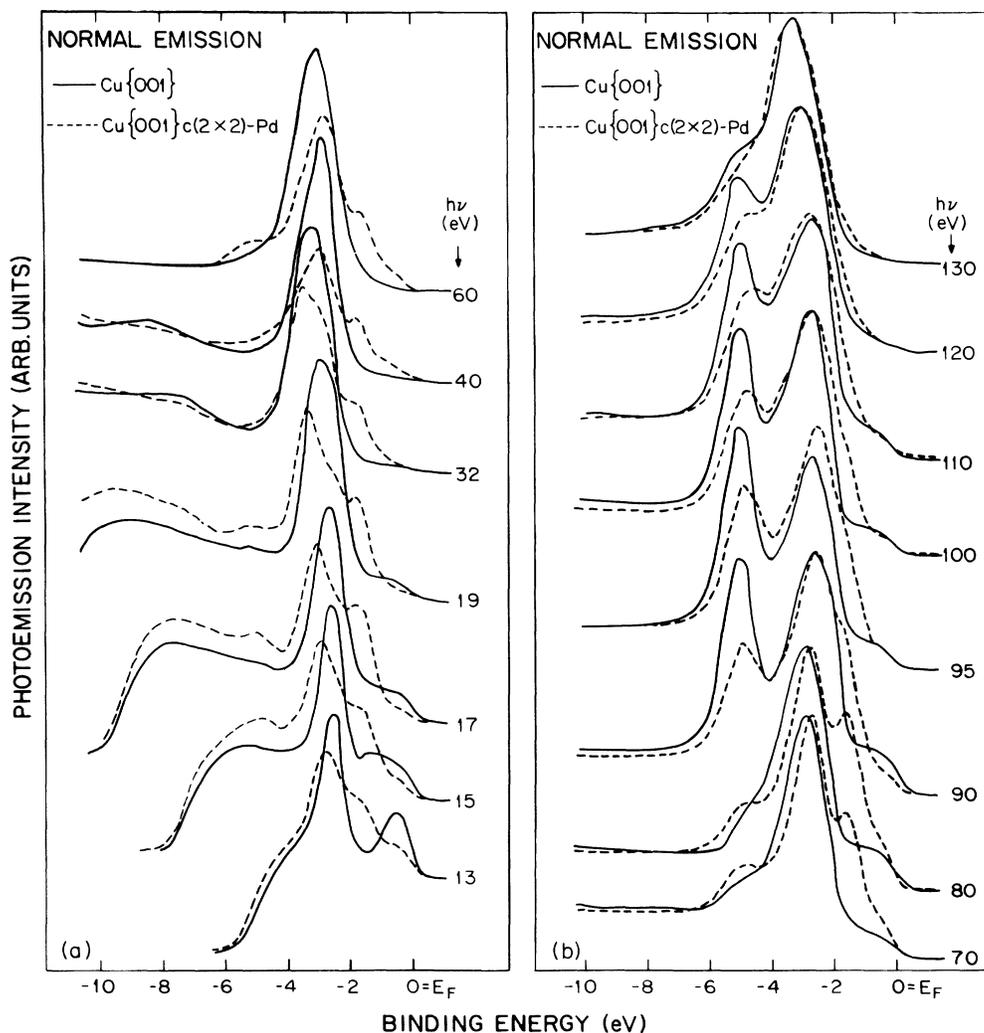


FIG. 3. Angle-resolved electron-distribution curves for normal emission from Cu{001} (solid) and Cu{001}c(2×2)-Pd (dashed) measured with photon energies between 13 and 130 eV.

Rao *et al.*⁹ with 21.2-eV photons on copper-rich (bulk) Cu-Pd alloys and attributed by these authors to Pd 4*d* electrons. The appearance of these same peaks in the EDC's of the Cu{001}c(2×2)-Pd structure is therefore an indication that the Pd and Cu atoms have bonded to one another as in the bulk alloys—a confirmation of the surface-alloy character unveiled by the LEED analysis. Furthermore, it is obvious from Fig. 3 that either peak exhibits little or no dispersion in the photon-energy range from 13 to 130 eV, a fact that is also consistent with the LEED results (more atomic than bulklike properties, in particular, no three-dimensional islands of Pd on the surface).

Two remarks about the -1.7- and the -4.8-eV peaks may be of interest. First, the doubts expressed earlier³ about the -4.8-eV peak being attributable to both Pd and Cu or only to Cu, for 17-eV photons, are clearly resolved by the appearance of this peak at 60-eV photon energy, where there is no contribution from Cu. Hence, this peak is undoubtedly Pd derived. Second, it is unlikely that the -4.8 eV peak has the same origin as the -1.7-eV peak (Rao *et al.*⁹ suggest that both peaks originate from Pd 4*d* electrons). The latter peak is clearly visi-

ble for all photon energies up to 130 eV and is not observed at or above this photon energy, where there is a Cooper minimum in the photoionization cross section of Pd 4*d* electrons.¹⁰ Hence, the association of the -1.7-eV peak with Pd 4*d* electrons is justified. The -4.8-eV peak may also disappear at or above 130-eV photon energy (it is difficult to know for sure, owing to the presence of Cu emission, as discussed below) but its photoionization cross section has a different behavior. This peak is observed for $h\nu < 22$ eV, is not observed for $22 < h\nu < 50$ eV, and is again observed at $h\nu = 60$ eV. For larger photon energies (80 eV and higher) Cu{001} exhibits a large surface state^{11,12} with about -5-eV binding energy. This Cu surface state is obviously reduced in intensity by the incorporation of Pd [Fig. 3(b)], but its permanence makes it difficult to ascertain the presence of Pd emission at -4.8 eV. Nevertheless, the different behavior of the photoionization cross sections indicate that the -4.8 eV and the -1.7-eV peaks have different origins.

A further confirmation of the alloy character of the Cu{001}c(2×2)-Pd phase is provided by the magnitude of the dispersion of the -1.7-eV peak with the parallel component k_{\parallel} of the wave vector. Figures 4 and 5 show

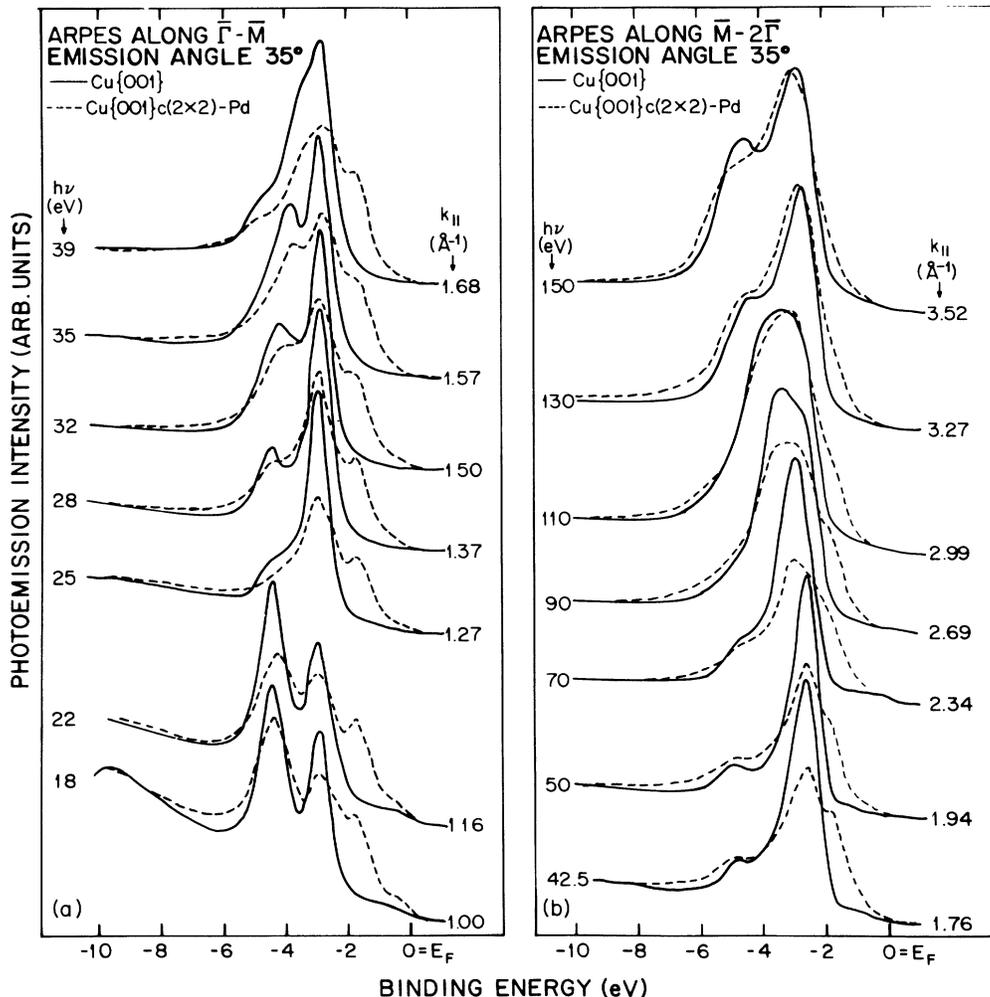


FIG. 4. Angle-resolved electron-distribution curves for emission at 35° along (a) the $\bar{\Gamma}-\bar{M}$ and (b) the $\bar{M}-2\bar{\Gamma}$ line of the surface Brillouin zone: Cu{001} (solid) and Cu{001}c(2×2)-Pd (dashed).

EDC's from both this phase and clean Cu{001} in different directions of the surface Brillouin zone: Fig. 4(a) ($h\nu$ from 18 to 39 eV, emission angle 35°) along $\bar{\Gamma}-\bar{M}$, Fig. 4(b) ($h\nu$ from 42.5 to 150 eV, emission angle 35°) along $\bar{M}-2\bar{\Gamma}$, Fig. 5(a) ($h\nu$ from 18 to 45 eV, emission angle 22°) along $\bar{\Gamma}-\bar{X}$, and Fig. 5(b) ($h\nu$ from 48 to 160 eV, emission angle 22°) along $\bar{X}-2\bar{\Gamma}$. The curves show that the -1.7 -eV peak has small dispersion: it is located at -1.7 eV at the $\bar{\Gamma}$ point, at about -1.6 eV at the \bar{X} point, and at -1.8 eV at the \bar{M} point,¹³ for an overall dispersion somewhat less than or equal to 0.2 eV. By contrast, the dispersion of the same Pd emission from ultrathin 1×1 overlayers of Pd on Ag{001} was measured to be about 0.3 eV by Smith *et al.*¹⁴ and calculated to be about 0.4 eV by Noffke and Fritsche.¹⁵ Thus, the dispersion observed on Cu{001} $c(2\times 2)$ -Pd is smaller than that found on overlayers of Pd, a fact indeed consistent with the alloy structure determined by LEED, as the Pd atoms in this structure are surrounded by Cu atoms and hence more isolated from one another than in 1×1 overlayers.

We consider next the -0.7 -eV peak. Graham¹⁶ observed this peak in EDC's from Cu{001} $c(2\times 2)$ -Pd measured with 21.2-eV photons in the vicinity of the \bar{M} point. We have systematically investigated the behavior of this peak by varying both photon energy and emission angle in order to follow both the \bar{M} point [Fig. 6(a)] and the \bar{X} point [Fig. 6(b)]. For $h\nu=22$ eV our curve reproduces Graham's curve well. In general, the -0.7 -eV peak can also be seen at low photon energies, for normal emission near the $\bar{\Gamma}$ point (Fig. 3), along $\bar{\Gamma}-\bar{M}$ (Fig. 4), along $\bar{\Gamma}-\bar{X}$ (Fig. 5), near the \bar{M} point, and finally near the \bar{X} point (Fig. 6) but cannot be seen in those EDC's where the presence of large emission from the Cu substrate (e.g., for $h\nu < 30$ eV in Fig. 3, for $h\nu=18$ and 45 eV in Fig. 5) makes the detection of the small Pd peak difficult and uncertain. Some indication of the origin of the peak at -0.7 eV may be obtained from densities of states (DOS) calculated for Cu₃Pd by total-energy band theory at the equilibrium lattice spacing.¹⁷ In contrast to pure Cu, both the Pd and the Cu in Cu₃Pd show a small peak in the DOS around the Fermi level separate from the d

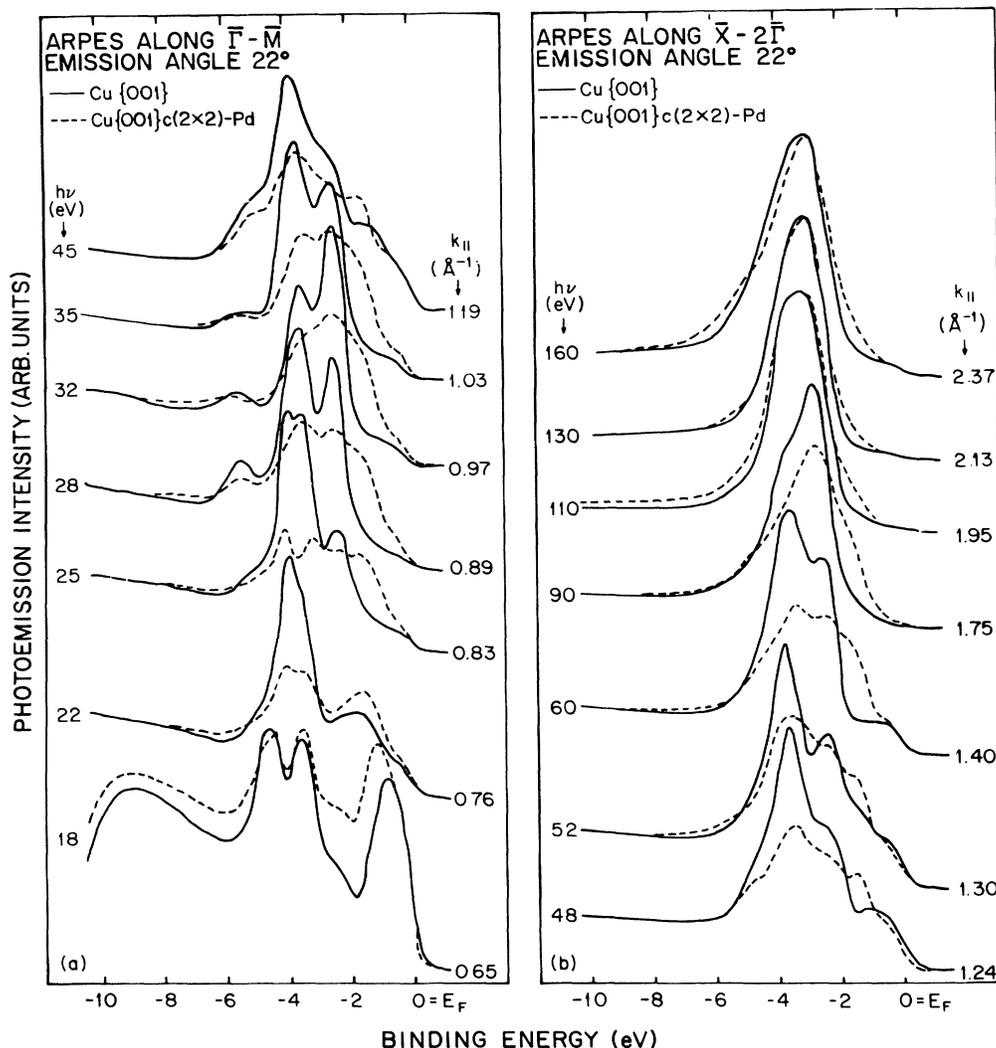


FIG. 5. Angle-resolved electron-distribution curves for emission at 22° along (a) the $\bar{\Gamma}-\bar{X}$ and (b) the $\bar{X}-2\bar{\Gamma}$ line of the surface Brillouin zone: Cu{001} (solid) and Cu{001} $c(2\times 2)$ -Pd (dashed).

bands and rising about 1 eV below the Fermi level. The Cu peak has considerably more strength.

V. CONCLUSIONS

The room-temperature reaction of Pd atoms with a clean Cu{001} surface leads to the formation of a surface alloy, Cu{001}c(2×2)-Pd. A LEED analysis determines the atomic structure as that of a mixed layer of 50% Pd and 50% Cu with slight buckling caused by the Pd atoms being 0.02 ± 0.03 Å outwards of the Cu atoms. LEED provides also the (qualitative) information that not all the Pd atoms react with Cu to form the mixed layer, at room temperature, so that an undetermined amount of Pd (in the sub-monolayer range) resides disordered either on or below the top layer of the Cu substrate. There is, however, no ordered Pd component beyond the mixed layer on the surface, at room temperature, hence the latter is a true surface alloy.

Photoemission confirms the alloy character of the Cu{001}c(2×2)-Pd phase by: (1) showing the appearance of Pd-induced features similar to those observed by

Rao *et al.*⁹ on Cu-rich Cu-Pd alloys, (2) showing little or no dispersion of the Pd features, and (3) in general, demonstrating a density of states which is Pd 5s-like (or Cu 4s-like) at the Fermi level E_F , with the Pd 4d-derived states well below E_F , thus suggesting that the Pd atoms do not form islands but rather react with the Cu atoms to produce the surface alloy.

It is interesting to note that the reaction of Pd atoms with a Cu{111} surface does not seem to produce a surface alloy. Pessa and Jylhä¹⁸ report rather the formation of one-layer-thick Pd islands, which then join one another to produce a 1×1 overlayer and ultimately an epitaxial film of Pd. This different behavior of Cu{001} and Cu{111} surfaces with regard to reaction with Pd is puzzling and deserves further scrutiny.

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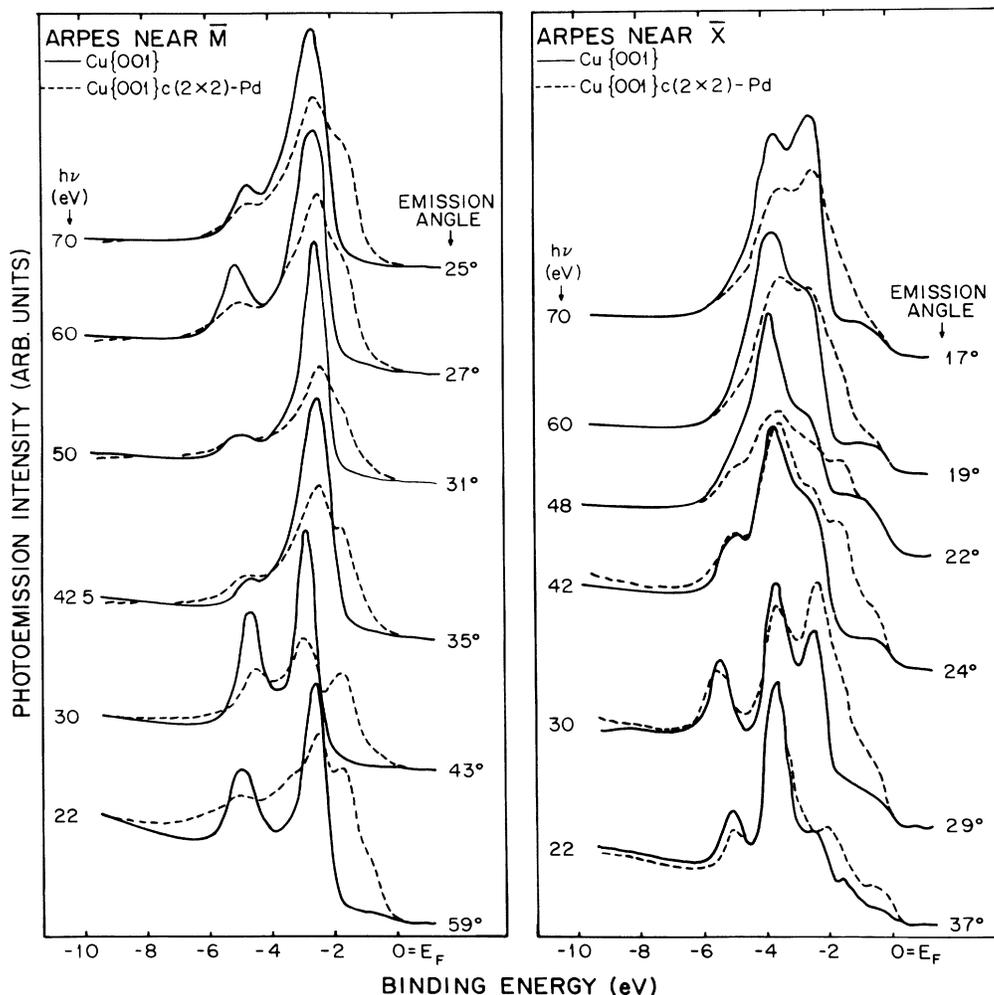


FIG. 6. Angle-resolved electron-distribution curves at the (a) \bar{M} and (b) \bar{X} point of the surface Brillouin zone for different emission angles and photon energies: Cu{001} (solid) and Cu{001}c(2×2)-Pd (dashed).

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