# Identification of Chemisorption Levels on Iridium by Field-Emission Spectroscopy

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The surface electronic structure of a stepped Cu(211) crystal was elucidated by angle-resolved photoemission spectroscopy. A surface state was found on the three-atom terraces, indicating that the terrace surface potential resembles that of a Cu(111) crystal surface. The $d$-band dispersion relations of Cu(211) were also found to resemble bulk copper closely. The observed enhanced reactivity of the stepped surface does not appear to arise from gross changes in the surface electronic structure.

Surface electronic states on low–Miller-index planar metal surfaces have received considerable theoretical attention, and experimental examples are known for Mo and W(100)[1] and Cu(111).[2] Until now, however, the detailed surface electronic structure of stepped crystals has received much less attention, in spite of long-standing interest in the chemical behavior of step sites, and no detailed theoretical predictions of surface states on stepped crystals are available. In this Letter, we report the first angle-resolved photoemission study of a stepped crystal surface: the (211) face of copper, which consists of three-atom terraces of (111) orientation separated by one-atom–high steps of (100) orientation. A surface state was found on this surface at $0.2 \pm 0.1$ eV below the Fermi energy ($E_F$). This state was characterized by both angle-dependent and photon-energy–dependent photoemission, and by direct comparison with the surface state at $0.3 \pm 0.1$ eV below $E_F$ on Cu(111).[3] From this study, we conclude that the Cu(211) surface state is associated with the Cu(111) terraces. The implications of this finding for the nature of the stepped-crystal potential are discussed below. In addition, preliminary experiments are reported that demonstrate the increased reactivity of a stepped Cu(211) crystal surface relative to a (111) surface.

Figure 1 depicts a segment of an ideal $(S)$-[3(111) ×(100)] surface.[4] Each terrace consists of three inequivalent atomic rows (labeled $A$, $B$, and $C$); thus only one-third of the surface atoms (in $C$-type rows) have the coordination of atoms at a (111) surface. Such a high step density might be expected to alter the surface electronic structure significantly. The purpose of this study was to provide information on this point.

Single crystals of copper were cut to within $\pm 0.5°$ of the (211) and (111) planes; the (111) crystal was used for comparison purposes throughout these experiments. The crystals were cleaned

and annealed *in situ*, and Auger analysis showed no surface contaminants within the limits of detectability (approximately 0.3 monolayers). Sharp LEED (low-energy electron diffraction) patterns were obtained from each crystal in a separate experiment chamber, with the characteristic $(S)$-[3(111) ×(100)] surface geometry evident on the Cu(211) crystal.

The photoemission experiments were conducted on the 8° branch line of beam line I at the Stanford Synchrotron Radiation Laboratory, using an experimental chamber described elsewhere[5]; photon energies in the range 8 eV $\leqslant h\nu \leqslant$ 35 eV were utilized. The incident radiation was highly (>97%) polarized in the horizontal plane, and the electron energy analyzer was fixed in this plane, accepting electrons emitted in a cone of 5° half-angle at an angle of 145° relative to the propagation direction of the photon beam. Variation of the electron-takeoff angle (and simultaneously the radiation polarization vector[6]) relative to the sample normal was achieved by rotating the crystal about a vertical axis. The total experimental resolution (monochromator plus electron ana-
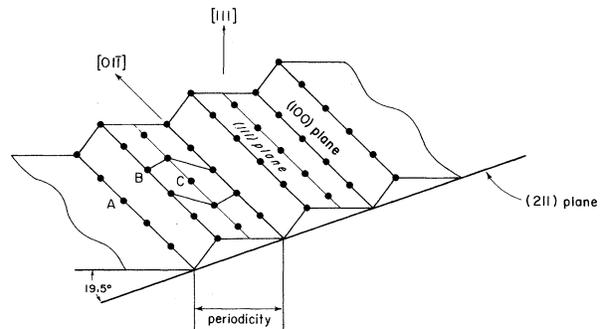


FIG. 1. A segment of an ideal Cu($S$)-[3(111) × (100)] surface, showing three-atom terraces of (111) orientation separated by monotonic steps with a (100) orientation.

lyzer) increased from ~0.17 eV at $h\nu = 8$ eV to ~0.26 eV at $h\nu = 35$ eV.

Figure 2(a) shows photoemission spectra taken as a function of the electron-takeoff angle $\theta$ (measured from the sample normal in the plane containing the [111] direction), with a photon energy of 11 eV. The (211) surface state appears as a peak at a binding energy of $0.2 \pm 0.1$ eV at $\theta = 20°$. As $\theta$ is increased or decreased from this value, the peak decreases in intensity and moves toward the Fermi energy, disappearing at $\theta = 10°$ and $30°$. These are the same characteristics exhibited by the surface state on Cu(111) [see Fig. 2(b)],[2,3] if a rotation of $\theta = 19.5°$ is first applied to correct for the fact that the [111] direction of the Cu(211) crystal lies at $19.5°$ relative to the (211) plane. We infer that the Cu(111) surface state at $0.3 \pm 0.1$ eV, which shows a maximum in both binding energy and intensity in *normal* photoemission,[2,3] is present in modified form on the (111) terraces of Cu(211), with maxima in these properties normal to the terraces; i.e., also along the [111] direction. This supports a model[7] in which the Cu(111) surface state is an energy band highly localized in real space arising primarily from near-surface Cu $p_z$-like atomic orbitals (where

[111] is the $z$-quantization axis). We note that this implies that photoelectrons originating from the Cu(211) surface state show very little or no refraction at the solid-vacuum interface.

While the Cu(211) and Cu(111) surface states are very similar, they are not identical. Certain differences are evident in Fig. 3, which compares photoemission spectra collected in the [111] direction, from the Cu(211) and Cu(111) crystals, for several photon energies. The (211)–surface-state binding energy is apparently slightly lower than that on the (111) surface state, as noted above. The intensity of the (211) surface state is also lower relative to the bulk band features. It is tempting to attribute this reduced spectral intensity to a smaller relative "area" of unperturbed (111) face on the stepped crystal. This interpretation can only be offered as tentative, however, pending further investigation, because of both the extremely high sensitivity of surface states to surface quality and because the macroscopic polarization of the light with respect to the surface planes[6] was different for the two experiments. The spectral intensity of the (211) surface state also decreased more rapidly with increasing photon energy than did the (111) surface state.

Turning to the bulk-derived features of the
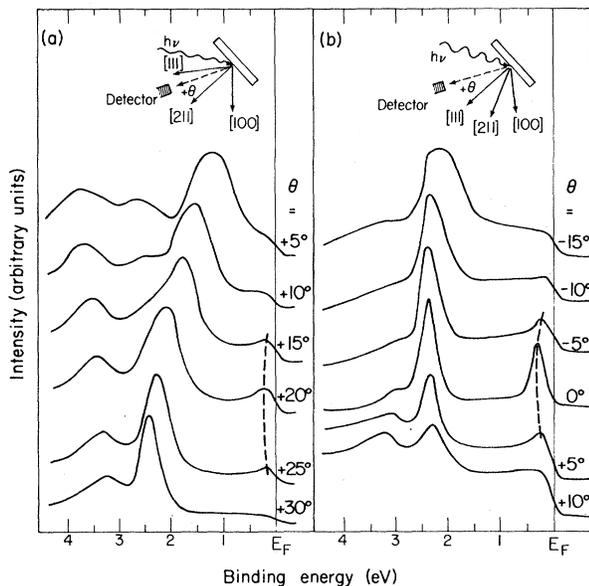


FIG. 2. Photoemission spectra of the valence-band region of copper taken as a function of the electron-takeoff angle $\theta$ (measured from the sample normal), with a photon energy of 11 eV, for (a) Cu(211); (b) Cu(111). The detailed experimental geometries are given in the insets; the radiation polarization vector lies in the plane depicted.
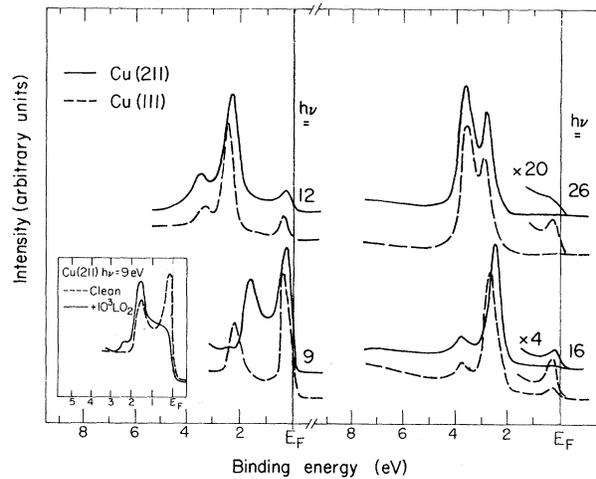


FIG. 3. Valence-band photoemission spectra obtained as a function of the incident photon energy for electrons propagating along the [111] direction of a Cu(211) crystal (solid curves) and a Cu(111) crystal (dashed curves). The inset shows spectra obtained at $h\nu = 9$ eV for electrons propagating along the [111] direction of a Cu(211) crystal both before (dashed curves) and after (solid curve) exposure to $10^3$ L (1 L$\equiv$ 1 langmuir = $10^{-6}$ Torr sec) of oxygen.

spectra, we find that the Cu(211) results are similar to those from Cu(111).[3] The Cu(211) bulk features show photoelectron refraction, and they can be interpreted within the direct-transition model (see Fig. 4 and below). Evidence for refraction is provided by comparing the angle-dependent spectra in Fig. 2(a) with those in Fig. 2(b). If refraction of the escaping photoelectrons at the solid/vacuum interface were unimportant, these two sets of data would be brought into registry by a shift of about $-20°$ in the angle from the surface normal for the Cu(211) data; i.e., the angle between the (211) and (111) axes. As seen in the figure, however, this is not the case. In fact, the main $d$-band peak in the Cu(211) spectra exhibits considerable dispersion in this angular range while that in the Cu(111) spectra remains essentially constant in binding energy.

Further evidence for refraction of bulk photoemission features appears in Fig. 3, in which



Wave vector
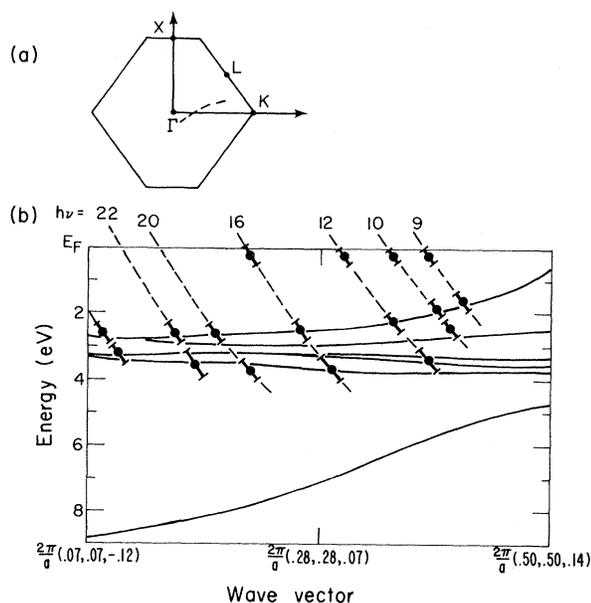
FIG. 4. (a) (110) projection of the three-dimensional Brillouin zone (BZ) of a fcc lattice. The dashed curve indicates the initial-state $\vec{k}$ points (determined by $\vec{k}$ conservation) which may contribute to photoemission in the [111] direction from a Cu(211) crystal, assuming the presence of photoelectron refraction at the surface. (b) Comparison of experimental peak positions for photoemission in the [111] direction from a Cu(211) crystal (solid curves in Fig. 3) to a theoretical band structure (Ref. 7). Free-electron final-state bands shifted down by the indicated photon energy are shown as dashed curves. Peak positions are shown as filled circles and bars denote peak full widths at half-maximum height.

photoemission spectra collected for electrons propagating in the [111] direction are compared for Cu(211) and Cu(111) surfaces. At the lowest photon energies ($h\nu = 9$ eV) the bulk features of the spectra are substantially shifted both because the refraction angle is larger for low-energy electrons and because the initial-state bands sampled at these photon energies happen to have a steep dispersion (see Fig. 4). At higher photon energies, these effects are smaller and the (211) and (111) spectra merge.

Figure 4 compares the peak positions observed for photoemission from the stepped Cu(211) crystal in the [111] direction with a calculated bulk band structure of copper.[8] The observed positions of bulk band features, interpreted on the direct-transition model,[9] agree well with the theoretical copper bulk band structure. Only two $d$-band peaks are typically observed; but considering the experimental peak widths and near degeneracy of the $d$ bands, all the $d$ bands may contribute at least weakly to the spectral area. The surface state is conspicuous in its separation from the bulk bands and in its nondispersive behavior.

As a final observation we report preliminary studies of the enhanced surface reactivity of Cu(211). On simultaneous exposure of a Cu(111) and a Cu(211) surface to $10^3$ L of $O_2$, the Cu(111) surface showed no detectable oxygen signal, while the Cu(211) surface showed $\sim 0.8$ monolayer of oxygen, as measured by the O($KLL$) Auger signal. Angle-resolved photoemission spectra along the [111] direction (inset, Fig. 3) showed that the (211) surface state had essentially disappeared (see the $h\nu = 9$ eV spectrum) while a feature appeared at a binding energy of $\sim 1.6$ eV that has been attributed to a Cu-O antibonding orbital.[10] The fact that the (211) surface potential supports a surface state on the (111) terraces tends to support theoretical predictions that there is no significant charge buildup at step sites in copper.[11] Hence, the enhanced reactivity of the (211) surface is apparently attributable to steric effects associated with the step sites, rather than unusual electronic structure. This might be expected by analogy with the chemistry of multinuclear transition-metal complexes—the catalytic is enhanced when a reactant molecule is sterically permitted to interact with several metal atoms in the transition state.[12]

In summary, we have found that the surface potential on (111) terraces of stepped Cu(211) sufficiently resembles that of Cu(111) to support a similar, but not identical, surface state. Other-

wise the electronic structure of the (211) surface
resembles the bulk band structure of copper.
This suggests that the enhanced reactivity of the
stepped surface—observed in this case for $O_2$—
may well arise more from steric effects due to
step-adsorbate geometry than from any particu-
lar electronic-structural property of these steps.

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# Phase Separation of the Electron-Hole Drop in ⟨111⟩-Stressed Ge

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We present a theoretical study of the electron-hole drop containing both "hot" and
"cold" carriers in ⟨111⟩-stressed Ge at $T = 0$. We predict that for certain values of the
stress this system phase separates into two degenerate Fermi liquids, one containing
"cold" and the other containing both "hot" and "cold" electrons. It should be possible to
verify this prediction experimentally.

When a ⟨111⟩ uniaxial stress is applied to Ge
the fourfold degeneracy of the conduction-band
minimum is lifted, three conduction valleys ris-
ing in energy while the fourth one is lowered.
Recent experiments.[1,2] have indicated that in an
electron-hole drop (EHD) in this system it is
possible for a substantial fraction of the elec-
trons to be present in the three upper valleys in
quasiequilibrium with the electrons in the lower
valley and with the holes. The relaxation time
for the so-called "hot" electrons associated with

the three upper valleys to decay into the lower
valley (the "cold" valley) was measured[1,2] to be
microseconds at moderate stresses. This value
is in agreement with a theoretical estimate of the
electron intervalley scattering time,[1] and com-
parable with, although smaller than, the total
lifetime of an EHD electron in the conduction
band. An independent observation of "hot" elec-
trons in the EHD in Ge in high magnetic fields
has also been reported.[3] Thus, there is substan-
tial evidence for the existence of both "hot" and