Surface States and the Photoelectron Spin Polarization of Fe(100)

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High-resolution angle-resolved photoemission spectra for Fe(100) are reported which identify and characterize surface states near the Fermi energy extending from $\bar{\Gamma}$ to $\bar{X}$ of the two-dimensional Brillouin zone. These results provide an experimental test of recent transition-metal surface electronic structure calculations and yield predictions relevant to spin-polarized photoemission from Fe(100).

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The study of intrinsic electronic and magnetic properties of transition-metal surfaces has attracted considerable interest recently. Theoretical studies of surface states on transition-metal high-symmetry crystal faces have been based primarily on energy-band calculations for thin slabs using a variety of approaches.[1-5] These calculations yield specific predictions related to surface electronic properties including surface band structure, surface states, layer density of states, and charge and spin densities. Some of these theoretical predictions can be subjected to direct experimental verification. As the number of computational methods and their predictions has expanded, the need for detailed experimental tests of the methods and results has also become more apparent.

This paper reports angle-resolved photoemission experiments conducted on an Fe(100) crystal surface. Our results provide a good description of surface emission properties for Fe(100) surfaces along the $\bar{\Gamma}$-$\bar{X}$ direction of the surface Brillouin zone. We find an encouraging correlation between surface emission features in our data and recent theoretical predictions[5] based on self-consistent calculations for a seven-layer Fe(100) slab. Our results also represent one of the first direct experimental tests of transition-metal surface electronic structure calculations and demonstrate the feasibility of such tests for this important class of metals in spite of complications arising from the high density of states characteristic of these metals.

Experiments reported here were conducted by using an angle-resolving photoemission spectrometer described previously.[6] The spectrometer is based on a commercial twin-pass cylindrical mirror analyzer which permits high-sensitivity Auger analysis in addition to angle-resolved ($\Delta\Omega = 4°$ or $12°$) photoemission experiments. The surface Brillouin zone is probed by rotating the sample or the angle-resolving aperture in the analyzer.

X-ray Laue techniques and spark erosion were used to align and cut 1-cm-diam iron disks 1 mm thick having a (100) crystal axis perpendicular ($\sim \pm 1°$) to the surface normal. Rods from which the crystal were cut were obtained from Leico Inc. Bulk impurities were reduced by heating the targets at ~ 800 °C for several weeks in a flowing hydrogen atomsphere. Samples were cleaned by repeated argon-ion sputtering (500 eV, 10 μA) and annealing (~ 800 °C) and were checked by using low-energy electron diffraction and Auger spectroscopy. Particularly clean surfaces are required to observe surface states on Fe(100). In our experiments, base pressures below 1×10^{-10} Torr were maintained (1×10^{-9} Torr noble-gas pressure during lamp operation), and total surface contamination (primarily oxygen) was judged to be below 1% of a monolayer.

Figure 1 illustrates the bulk band structure of iron[7] along Γ-Δ-H of the three-dimensional Brillouin zone with corresponding angle-resolved energy-distribution curves (AREDC's) taken at normal emission along the (100) direction. Before discussing AREDC's which exhibit surface emission features we focus on the bulk band structure of iron. In previous experiments, reported elsewhere,[8] we have determined the band structure and exchange splitting for iron along Γ-Σ-N using a (110) crystal surface. In that work we found the calculated band structure[7] to be in good agreement with experimental data which we interpreted on the basis of a direct transition model and a single free-electron final band. The same final band accounts for primary features in AREDC's for the (100) face. Binding energies corresponding to peaks in the normal-emission spectra are plotted on the band structure with $k_\perp$ values determined by assuming direct transitions to the free-electron final band. Final band energies are plotted to the right of the band structure. This result establishes the region of the bulk Brillouin

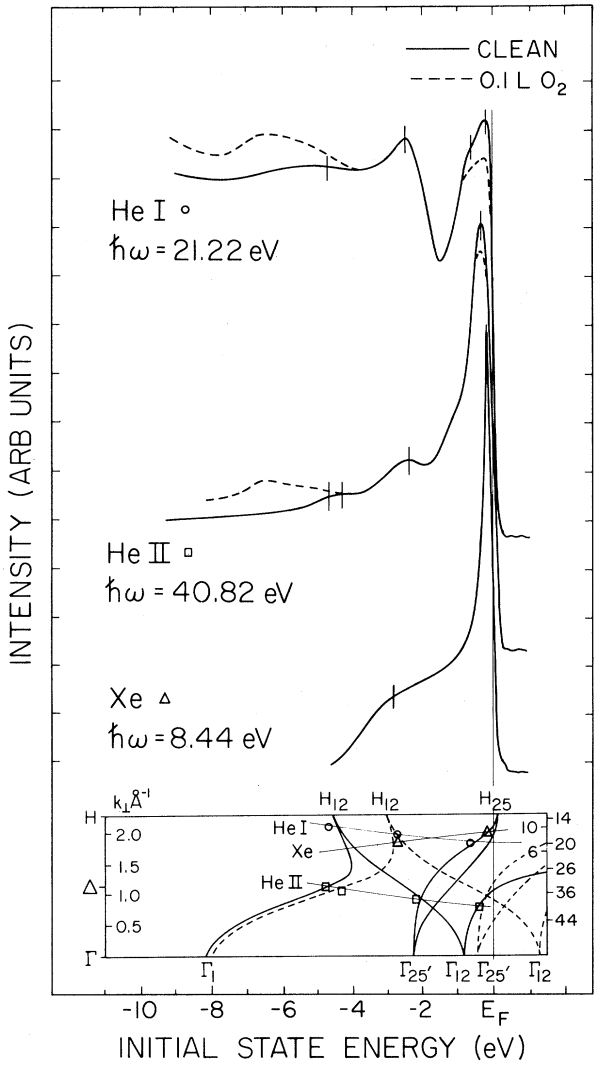

FIG. 1. Normal-emission AREDC's for Fe(100) at Xe, He I, and He II photon energies. Solid curves represent clean-surface data; dashed curves show effects due to 0.1 L of oxygen. Inset shows calculated bulk energy bands along Γ-H (Ref. 7) and points obtained from the AREDC's by using a direct interband transition model. Final band energies above E_F are shown to the right of the inset. Resolution: $\Delta E \sim 100$ meV, $\Delta\Omega \sim 4°$.

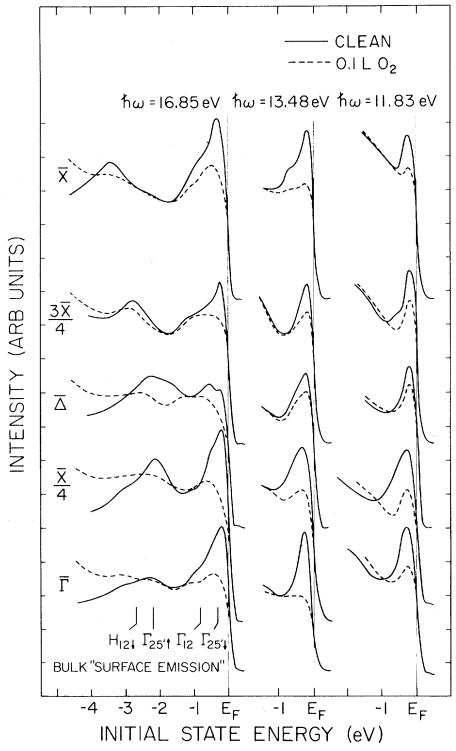

FIG. 2. AREDC's for Fe(100) at Ne I, Ar I, and Ar II photon energies. Solid curves represent clean-surface data; dashed curves show effects due to 0.1 L of oxygen. Each pair of curves corresponds to a location of the surface Brillouin zone along $\bar{\Gamma}$ to $\bar{X}$. The location of bulk and surface emission features at $\bar{\Gamma}$ (normal emission) are shown in the lower part of the figure. Resolution: $\Delta E \sim 100$ meV, $\Delta\Omega \sim 4°$.

zone probed at a given photon energy. Also shown in Fig. 1 is the sensitivity of peaks resulting from bulk direct transitions to small doses of oxygen ~0.1 L (1 L = 1×10^{-6} Torr sec). The sensitivity of AREDC features resulting from primarily bulk-band direct transitions is low in comparison with surface photoemission features as illustrated in Fig. 2.

One of the better opportunities to probe surface states on Fe(100) occurs at photon energies for which bulk transitions to the free-electron final band do not occur. A specific region of the bulk Brillouin zone meeting this condition is found at H. Callaway and Wang's band calculation places the Δ_2' and Δ_5 bands above E_F at H and this result is supported by Fermi surface data[9] which show that the H-centered majority-spin hole pockets are larger than their calculations predict. The nearest initial-state band around H in the bulk Brillouin zone which can contribute to AREDC's via direct transitions is the minority-spin H_{12} band which lies at -3.0 eV. Fortunately, three noble-gas resonance lines (Ne I, $\hbar\omega = 16.85$ eV; Ar I, $\hbar\omega = 11.83$ eV; and Ar II, $\hbar\omega = 13.48$ eV) probe k space near H in normal emission. These lines permit high-resolution (~50 meV) angle-resolved photoemission studies of the surface electronic structure of Fe(100).

Figure 2 shows selected AREDC's covering the surface Brillouin zone of Fe(100) along $\bar{\Gamma}$-$\bar{X}$. The three photon energies probe bulk bands near H in

the bulk Brillouin zone where the only direct interband transitions allowed are from the H_{12} subbands with binding energies of 3.0 and 4.5 eV. Features in AREDC's corresponding to lower binding energies must be due to surface states or surface photoemission. Surface emission is greatly decreased by chemisorbing 0.1 L (approximately 0.1 monolayer) of oxygen as shown in Fig. 2. Coverages are estimated from oxygen Auger line intensities, which correlate with gas doses. The coverages are low enough to ensure that ordered structures are not formed.

The AREDC's corresponding to oxygen-coated surfaces exhibit features which correlate with bulk states at high-symmetry points in the bulk Brillouin zone where the bands tend to be very flat. This is not surprising because when no interband transitions are allowed, surface emission dominates and "band-gap" emission corresponding to k values with high densities of states is expected. There is also good evidence for direct transitions for the $H_{12\downarrow}$ band in these AREDC's. Dispersion of the feature associated with $H_{12\downarrow}$ is consistent with the interpolated bulk band structure along the azimuth corresponding to sweeping from $\bar{\Gamma}$ to $\bar{X}$ in the surface Brillouin zone.[10]

Two theoretical calculations of Fe(100) surface electronic properties are available to serve as a basis for discussing the results of Fig. 2. Dempsey, Kleinman, and Caruthers[1] have reported surface energy bands for a 41-layer Fe(100) slab obtained from a linear combination of atomic orbitals calculation with matrix-element parameters based on a bulk band calculation. Wang and Freeman[5] have recently reported an *ab initio* self-consistent band calculation based on a seven-layer Fe(100) slab. Both calculations are for magnetic slabs.

These two calculations exhibit similar features, but also distinct differences: There are strong general similarities between corresponding surface energy bands when comparing equivalent spin and symmetry (even or odd) bands along a surface zone direction. The 41-layer parametrized calculation is able to clearly distinguish surface-state bands which split off from the continuum of states for the slab. In the seven-layer *ab initio* calculation, surface states are designated by flags on bands corresponding to a high percentage of first- and second-layer charge density. We have chosen the seven-layer bands on which to overlay our experimental results because they are much less complex than the

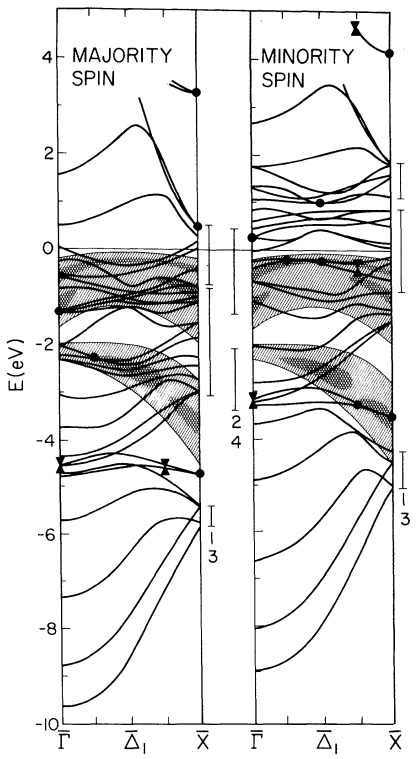

FIG. 3. Surface energy bands for Fe(100) (Ref. 5). Dots flag bands having a high percentage of charge density in first and second layers. Shaded areas show regions of the surface Brillouin zone where strong chemisorption effects are observed in AREDC's. Heavy shading corresponds to strong quenching of AREDC features by chemisorption.

41-layer bands and therefore provide a less cluttered background. It is appropriate to comment here that recent photoemission results for Ni(110) surfaces[11] have shown that the magnetic exchange splitting of surface and bulk electronic states are equivalent (no magnetic dead layers at the surface). This result justifies comparison of our experimental results with spin-polarized slab calculations.

Figure 3 illustrates even-symmetry surface energy bands for Fe(100) along $\bar{\Gamma}$-$\bar{X}$ from Ref. 5. Superimposed on these bands are shaded regions corresponding to differences between our measured clean-surface AREDC's and corresponding contaminated-surface AREDC's. The degree of shading gives a rough indication of the magnitude of the difference. The shading for both majority- and minority-spin panels of Fig. 3 is the same (our experiment does not discriminate spin) and we have not shown the corresponding two odd-symmetry panels for simplicity. (It turns out

that the two odd-symmetry panels from the self-consistent calculation do not exhibit bands along $\bar{\Gamma}$-$\bar{X}$ which are noted as having a high percentage of first- and second-layer charge density.) In addition, our source is unpolarized and we cannot make any meaningful statements regarding symmetry difference.

Our results illustrate a rather encouraging correlation between calculated surface electronic structure and experimental data. The parametrized calculation predicts an even-symmetry minority surface state extending from near $\bar{\Gamma}$ to about $\bar{X}/2$ before passing above the Fermi energy. The *ab initio* calculation predicts a similar surface state just below E_F, but extending the entire distance to $\bar{X}$. In nearly every region of the surface Brillouin zone where a surface band is predicted by the *ab initio* calculation, we find evidence of surface-state emission.

The results shown in Figs. 1 and 2 also allow us to make some predictions regarding spin-polarized photoemission experiments[12] for Fe(100) surfaces. Bulk interband transitions to the free-electron final band cannot occur at photoemission threshold characterized by the condition $\hbar\omega = \varphi$, where φ is the Fe(100) surface work function (~ 4.4 eV). Bulk emission requires bulk initial states at $k_\perp \sim 1.5$ Å^{-1} along the Δ line of the bulk Brillouin zone (see Fig. 1). Our experimental results[8] for Fe(110) have shown that $\Gamma_{25\downarrow} = 0.27$ eV and $\Gamma_{12\uparrow} = 0.78$ eV, indicating that Callaway and Wang's calculated bulk bands for Fe are quite accurate. The AREDC's shown in Fig. 1 also support this conclusion. We can therefore say with a high degree of confidence that threshold emission from Fe(100) will involve primarily surface emission from $\bar{\Gamma}$ in the surface Brillouin zone.

The surface band calculations predict both minority- and majority-spin bands at $\bar{\Gamma}$ and E_F, but minority-spin bands dominate first-layer projected densities (Fig. 2 of Ref. 5). Therefore, a negative electron spin polarization (ESP) should be observed *at threshold* for Fe(100). Above threshold, an abrupt sign change in ESP is expected because of transitions from the $\Delta_{25\downarrow}$ bands. It is interesting to note that similar ESP behavior has been observed for Ni(100) surfaces[12] and attributed to surface-state emission.[6,13]

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[1]D. G. Dempsey, L. Kleinman, and E. Caruthers, Phys. Rev. B 12, 2932 (1975), and 13, 1489 (1976), and 14, 279 (1976).

[2]D. G. Dempsey and L. Kleinman, Phys. Rev. B 18, 1270 (1978), and Phys. Rev. Lett. 39, 1297 (1977).

[3]C. S. Wang and A. J. Freeman, Phys. Rev. B 19, 793, 4930 (1979), and 21, 4585 (1980).

[4]F. J. Arlinghaus, J. G. Gay, and J. R. Smith, Phys. Rev. B 21, 2055, 2201 (1980), and Phys. Rev. Lett. 42, 332 (1979).

[5]C. S. Wang and A. J. Freeman, Phys. Rev. B 24, 4364 (1981).

[6]J. L. Erskine, Phys. Rev. Lett. 45, 1446 (1980).

[7]J. Callaway and C. S. Wang, Phys. Rev. B 16, 2095 (1977).

[8]A. M. Turner and J. L. Erskine, Phys. Rev. B 25, 1 (1982).

[9]D. R. Baraff, Phys. Rev. B 8, 3439 (1973); A. V. Gold, L. Hodges, P. T. Panonsis, and D. R. Stone, Int. J. Magn. 2, 357 (1971).

[10]S. D. Kevan, P. S. Wehner, and D. A. Shirley, Solid State Commun. 28, 517 (1978).

[11]W. Eberhardt, E. W. Plummer, K. Horn, and J. Erskine, Phys. Rev. Lett. 45, 273 (1980).

[12]Spin-polarized photoemission experiments have been conducted on Ni surfaces [W. Eib and S. F. Alvarado, Phys. Rev. Lett. 37, 444 (1976)] and on Fe(111) surfaces [W. Eib and B. Reihl, Phys. Rev. Lett. 40, 1674 (1978)] but apparently not on the Fe(100) surface.

[13]D. G. Dempsey and L. Kleinman, Phys. Rev. Lett. 39, 1297 (1977); D. G. Dempsey, W. R. Grise, and L. Kleinman, Phys. Rev. B 18, 1270 (1978).