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Magnetic surface states on Fe(001)

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The direct observation of magnetic surface states on Fe(001) is reported. A spin-polarized angle-resolved photoemission study identifies a minority surface resonance at $\bar{\Gamma}$ (2.40-eV binding energy) and a minority surface state at $\bar{X}$ (2.25-eV binding energy) in the surface Brillouin zone. The majority counterpart of the minority surface resonance is not observed. Good agreement with 7- and 13-layer full-potential linearized-augmented-plane-wave calculations is found for the minority $\bar{\Gamma}$ to $\bar{X}$ surface band. In addition, the 13-layer slab calculation is found to more correctly model the decay of the surface resonance into the bulk in contrast to the 7-layer slab where size effects play a role.

The magnetic properties of surfaces and thin films is currently an area of great interest.[1,2] The low dimensionality of these systems gives rise to unique chemical and physical characteristics. Changes in coordination, symmetry, and lattice dimensions result in new properties which are intimately related to the surface and interface electronic states. Early studies[3] on nickel, iron, and cobalt films stimulated interest by suggesting that the surface layers were magnetically dead. However, this was later traced to surface contamination. Later photoemission studies[4] of clean surfaces of nickel identified, on the basis of symmetry arguments and temperature dependence, what were believed to be exchange-split surface states, providing strong evidence for surface magnetism. Similar experiments[5] on Fe(001) identified several features associated with the surface which first-principles calculations[6] have demonstrated are consistent with a ferromagnetic rather than paramagnetic order. The theoretical work also predicted an enhanced surface moment. In this paper we directly identify minority spin surface features on Fe(001) using spin-polarized angle-resolved photoemission. Comparison is made with spin-polarized surface electronic structure calculations.

The spin-polarized photoemission experiments reported here were carried out on a new apparatus which will be described in detail elsewhere.[7] Briefly, spin detection is achieved with a compact low-energy spin detector[8] and uses light provided by the U5 vacuum ultraviolet (VUV) undulator at the National Synchrotron Light Source.[9] The angular resolution of the hemispherical analyzer[10] was $\pm 1.5°$ and the combined photon and analyzer energy resolution was 0.35 eV. The Fe(001) crystal[11] was manufactured in the form of a picture frame with each leg along a ⟨100⟩ direction and magnetized using a coil wound around one leg. The crystal was cleaned by repeated argon-ion bombardment and annealing cycles. The surface contamination level was monitored initially using Auger electron spectroscopy and in the final stages using photoelectron spectroscopy. The surface remained clean for only a short period, contamination peaks in the photoemission spectra became visible after ~20 min. However, flashing the sample to 750 °C every 15 min kept it free from contamination for extended periods. Each spectrum shown here was collected in ~35 min.

The experimental findings are compared with self-consistent electronic structure calculations for 7- and 13-layer Fe(001) films. The all-electron full-potential linearized-augmented-plane-wave (FLAPW) method using the spin-polarized exchange-correlation potential of von Barth and Hedin has been employed.[12] The results of these calculations are essentially in agreement with those previously reported for a 7-layer film.[6] However, certain aspects are more correctly represented by the thicker film as will be shown below.

Figure 1 shows the spin-resolved spectra for the clean surface at normal emission ($\vartheta_e = 0°$) and $\vartheta_e = 19°$, corresponding to the $\bar{\Gamma}$ and $\bar{X}$ points, respectively, in the surface Brillouin zone. The photon energy was 52 eV and the light was incident at $\vartheta_i = 70°$ (with respect to the surface normal) and in the (100) plane. The minority (0.3 eV) and majority (0.7 and 2.6 eV) peaks at normal emission [Fig. 1(a)] are derived from relatively flat bulk bands near Γ in the Γ-Δ-H direction of the bulk Brillouin zone. At normal emission, selection rules only allow initial states of Δ_1 and Δ_5 symmetry; Δ_1 when the electric vector lies perpendicular to the surface, Δ_5 when it is parallel. At the angle of incidence employed in this work the Δ_1 majority peak (0.7-eV binding energy) is relatively intense compared to the Δ_5 exchange split bands (0.3 and 2.6 eV). These Δ_5 peaks were found to be stronger at small angles of incidence in agreement with previous work.[13] The rapidly rising intensity below ~5-eV binding energy [Fig. 1(a)] is due to the presence of a relatively intense s/p band at these energies. At this photon energy ($h\nu = 52$ eV) the d-band intensity is greatly reduced prior to the $3p$ threshold and there also appears to be strong coupling to the final state, leading to the intense s/p band emission. This band disperses towards the Fermi level in the $\bar{\Gamma}$-$\bar{\Delta}$-$\bar{X}$ direction and is at ~3.3-eV binding energy at $\bar{X}$ [Fig. 1(b)].

The peak at 2.4-eV binding energy in the clean $\bar{\Gamma}$ minority spectrum [Fig. 1(a)] occurs at the same binding energy independent of photon energy and is highly surface sensitive, being quenched by small quantities of oxygen. Only weak intensity changes are observed in the majority spectrum. The measured dispersion of this surface feature, derived from spin-integrated data, is shown in Fig. 2. The calculated dispersion of the surface band from the

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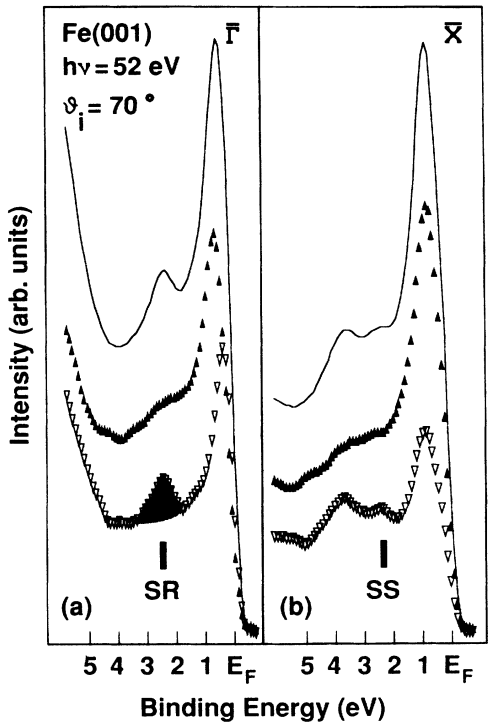

FIG. 1. Spin-polarized photoemission spectra for clean Fe(001) taken at the (a) $\bar{\Gamma}$ and (b) $\bar{X}$ points of the surface Brillouin zone. Spin integrated (line) together with the minority (▽) and majority (▲) components are shown. SR and SS mark the minority surface resonance and surface state, respectively. The attenuation of the minority surface resonance following a 0.1-L oxygen exposure (where 1 L $=10^{-6}$ Torr sec) is shown by the shaded region.

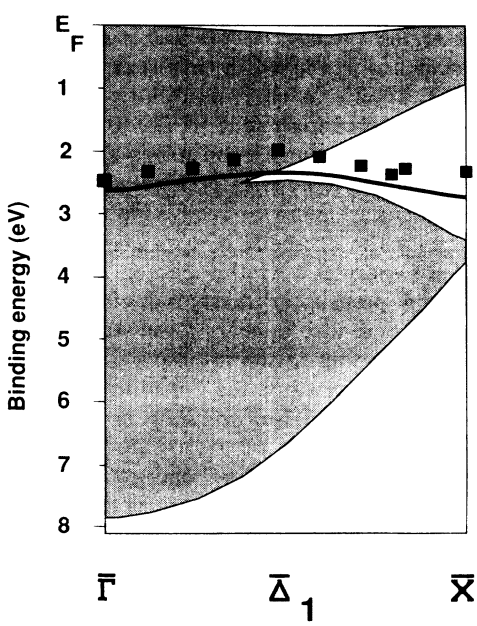

FIG. 2. Experimental dispersion of the minority surface band (■) compared to the theoretical dispersion determined from the 13-layer FLAPW calculation (thick solid line). The calculated minority bulk projected bands are shown by the shaded region.

13-layer slab calculations is also included in Fig. 2. It can be seen that there is reasonable agreement with the experimentally determined dispersion. There is a gap in the projected spin density of states at $\bar{X}$ but not at $\bar{\Gamma}$, and therefore the surface-derived feature represents a surface resonance and a surface state at $\bar{\Gamma}$ and $\bar{X}$, respectively. The $\bar{X}$ minority surface state is observed at ~2.25-eV binding energy [Fig. 1(b)]. Minority surface features are predicted to lie at 2.57- (2.75-) eV binding energy at $\bar{\Gamma}$ and 2.65 (2.60) eV at $\bar{X}$ in the 13- (7-) layer ground-state calculations. Given that there is no reason to expect exact agreement with the excitation spectra the close correspondence between experiment and theory may well be fortuitous. Even so, it would seem that the FLAPW method models the surface electronic structure of Fe(001) reasonably well.

Features at similar energies have previously been observed in spin-integrated work[5] at lower photon energies, and although the binding energies were in general agreement with theory, the $\bar{\Gamma}$ surface feature could not be unambiguously assigned to a minority or majority feature. Further, a peak at ~3-eV binding energy at $\bar{\Gamma}$ was observed in that work which is not evident in Fig. 1(a). Spectra with small levels of carbon contamination, however, do have a peak at this energy.

Majority surface features are predicted to lie ~1.7 and 1.5 eV below the minority states at $\bar{\Gamma}$ and $\bar{X}$, respectively, in both the 13- and 7-layer calculations. The $\bar{X}$ majority state would be expected to lie very close to the s/p band and may well be obscured by it. However, the energy range of the spectra shown in Fig. 1(a) is such that the majority state at $\bar{\Gamma}$ should be observable at ~4-eV binding energy. It is evident though that this state is not resolvable above the background. This is unlikely to be due to cross-section effects since the peaks are an exchange split pair with similar $s/p/d$ composition. Instead the weakness of the majority component may well reflect a broadening of the peak due to a combination of effects. Lifetime broadening of the majority peaks compared to their minority counterparts has recently been observed in studies of $p(1\times1)$O/Fe(001),[14] where it was suggested that the effect reflected the difference in occupation of the spin states. Another effect, of particular importance in this case,[15] which would also broaden the majority compared to the minority peaks is that the majority bulk states which couple to the surface features are spread over a larger energy range than their minority counterparts.

The $\bar{\Gamma}$ minority surface resonance is of $d_{z^2}(+s/p_z)$ character and is split off from the bulk band at the point where the d bands hybridize with the s/p band ~ $\frac{2}{3}$ to $\frac{3}{4}$ of the way from Γ to H. The d_{z^2} character can most clearly be seen in Fig. 3 where the charge density for this minority state is plotted in the (110) plane. The density in the first two layers amounts to ~52% of the total (normalized to the half-space $z>0$) although there is still appreciable intensity in the central layer. A similar trend is observed for the majority state with ~44% in the top two layers. The layer oscillatory nature of the wave function appears to be a real effect and related to the fact that these states are derived from bulk bands not at the zone center or edge. The period of the oscillations and the

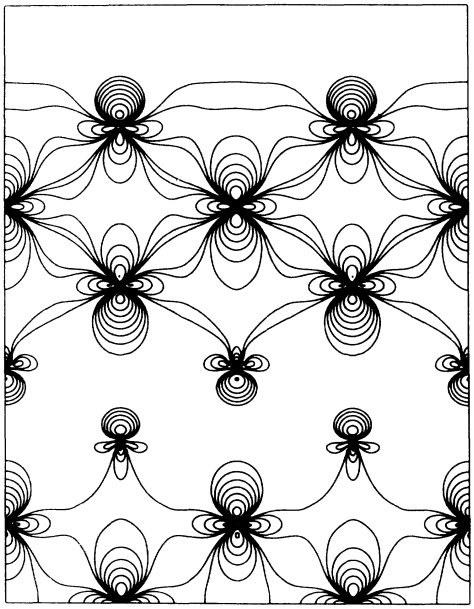

FIG. 3. Wave function squared of the minority surface resonance at $\bar{\Gamma}$ for a 13-layer Fe(001) slab plotted in the (110) plane perpendicular to the surface. The units are $1\times10^{-3}e/(\text{a.u.})^3$ and contour lines differ by a factor of 2.

difference between the calculated majority and minority states are consistent with the states being derived from the maxima of the Δ_1 bulk bands. It is interesting to note that in the 7-layer calculation, a similar phenomena is observed, but now ~85% of the minority state, compared to ~48% of the majority state, is in the top two layers. The ~10% difference in the dominant perpendicular wave vectors of the majority and minority wave functions is such that the majority states from opposite sides of the 7-layer film can interact much more strongly than the minority ones. This increased interaction results in the weight being distributed more uniformly throughout the 7-layer film, leading to the possible conclusion that the minority state is significantly more localized than the majority one. Although such an observation correlates well with the weak intensity of the majority surface resonance compared to the minority, the 13-layer calculation demonstrates that this is purely an artifact of the film thickness. Thus, although the two calculations differ little in most respects, the attenuation of the resonances is incorrectly modeled by the 7-layer film. While finite-size effects are undoubtedly still present in the 13-layer calculations, we believe that the basic features of the states are more reasonably well described.

The $\bar{X}$ surface state is mostly *d*-like with, however, a significant mixing of *s* character. It is split off the lower edge of the continuum gap (Fig. 2). In keeping with its more localized nature, 89% of the density occurs in the top two layers.

In summary, spin-polarized surface electronic states have been directly observed and their binding energies are found to be in general agreement with the expectations of thin-film calculations. Although the calculated magnetic moments, band dispersion, etc. for the 7- and 13-layer slabs are essentially the same, the attenuation of the $\bar{\Gamma}$ surface resonance is better modeled by the 13-layer slab.

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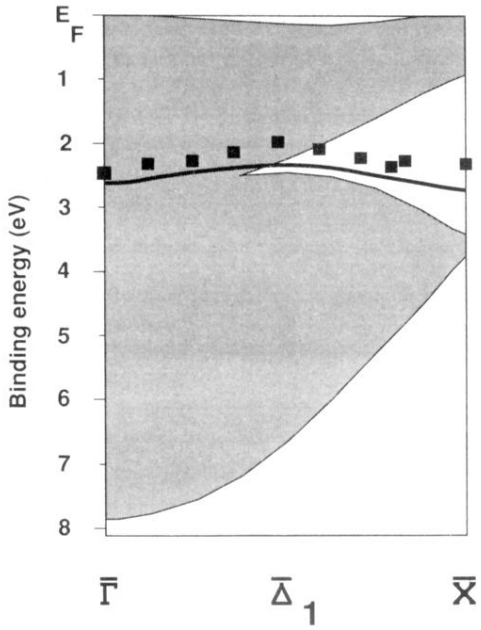

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