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Magnetic exchange splitting and band dispersion of surface states on Fe(100)

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We have determined the band dispersion and magnetic exchange splitting of odd-symmetry Shockley surface states along the $\bar{\Delta}$ and $\bar{\Sigma}$ lines in the surface Brillouin zone of Fe(100) using angle-resolved photoemission. The average surface exchange splitting along the $\bar{\Delta}$ and $\bar{\Sigma}$ lines is larger than the average bulk value. Surface-state band dispersion and binding energies along $\bar{\Sigma}$ are in good agreement with recent slab calculations.

Considerable progress has been made recently in addressing questions pertaining to the role of magnetism in surface phenomena. Accurate computational methods applied to ferromagnetic films have yielded specific predictions including the surface magnetic moment, exchange splitting, spatial character, and energy-band dispersion of surface states.[1-6] These surface calculations provide a new means of testing and improving *ab initio* self-consistent computational techniques and also provide the framework needed to understand and predict surface phenomena associated with magnetic materials. A recent review article covering itinerant-electron surface magnetism summarizes the broad range of current issues in the field of surface magnetism and provides references to the large body of literature on the subject.[7]

Several experimental techniques are capable of probing directly or indirectly surface electronic and magnetic properties. Angle-resolved photoemission, including experiments which resolve spin, has provided detailed information about bulk[8-10] and surface[11-15] electronic properties of magnetic metals and thin magnetic films.[16] The bulk[5,9] and surface[11-14] electronic properties of nickel in particular have now been extensively studied. However, the bulk[10] and surface[15] electronic properties of iron have not been extensively studied, even though iron would appear to provide a very attractive test case for surface calculations. Nickel is judged less suitable for such tests because of the significant disagreements between state of the art calculations of the bulk electronic structure and the band structure and magnetic exchange splitting determined by angle-resolved-photoemission experiment.[8,9] We have recently completed a comprehensive experimental study of the bulk electronic properties of ferromagnetic iron.[17] Based on this, we have also been able to obtain a direct experimental determination of the magnetic exchange splitting and band dispersion of surface states on crystal faces of iron. These results provide an extremely sensitive test of the new computational techniques being applied to magnetic surfaces.

In this paper, we report initial results of our angle-resolved-photoemission studies of the Fe(100) surface which yield the exchange splitting and band dispersion of surface states and surface resonances along $\bar{\Delta}$ and $\bar{\Sigma}$ lines of the two-dimensional Brillouin zone.

The experiments were conducted at the Synchrotron Radiation Center in Stoughton, Wisconsin, using a new angle-resolving photoelectron spectrometer which is described in detail elsewhere.[17] The instrument provides low-energy electron diffraction, Auger spectroscopy, and other necessary sample-cleaning and characterization capabilities, and maintains a 10^{-11}-Torr range of pressures necessary for surface studies. Our sample-preparation and cleaning procedures utilize standard techniques which have been discussed elsewhere.[10,15] The angle-resolving electron optics are mounted on a two-axis goniometer which permits photoelectron detection along any axis which intersects the sample. Apertures in the electron optics establish a $\pm 1.2°$ angular resolution, and for the experiments reported here, the energy resolution (monochromator plus analyzer) was maintained at 100 meV. A versatile sample manipulator provides rotation and tilt motions required to obtain *s*- and *p*-polarized incident radiation.

The calculated surface band structure of ferromagnetic metals along symmetry lines in a particular two-dimensional Brillouin zone tends to be rather complicated. However, two-dimensional magnetic bands can be presented in a simplified form by decomposing bands into four sets for each symmetry line, each set corresponding to a specified value of spin (majority and minority) and spatial symmetry (even or odd) about the symmetry line. Figure 1 displays the results of two independent calculations[1,4] using different methods for the Fe(100) surface. The upper two sets display odd-symmetry majority- and minority-spin surface bands along the $\bar{\Sigma}$ direction. These bands were obtained using a parametrized tight-binding calculation applied to a 41-layer film.[1] The lower two sets display corresponding results obtained using an *ab initio* self-consistent calculation applied to a seven-layer film.[4] The odd-symmetry two-dimensional bands along the $\bar{\Sigma}$ line present one of the most striking examples of an exchange-split surface state on an iron surface. For this reason, most of the discussion in this paper centers on this specific direction and band symmetry. Other iron surfaces, surface-zone directions, and initial-state symmetries will be discussed in a more comprehensive account of our work.[18]

Referring first to Fig. 1(a) (41-layer calculation), one can see that a wide gap opens up at $\bar{\Gamma}$ and is pinched off along the $\bar{\Sigma}$ line for both majority- and minority-spin

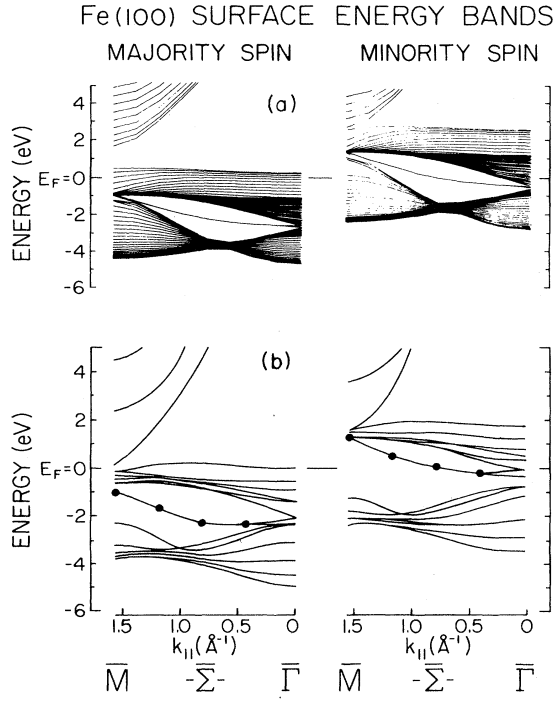

FIG. 1. Calculated odd-symmetry surface bands along the $\bar{\Sigma}$ line of the two-dimensional Brillouin zone. (a) Parametrized calculation for a 41-layer Fe(100) film (Ref. 1); (b) self-consistent calculation for a seven-layer Fe(100) film (Ref. 4). Solid circles identify surface states in the self-consistent-band calculation.

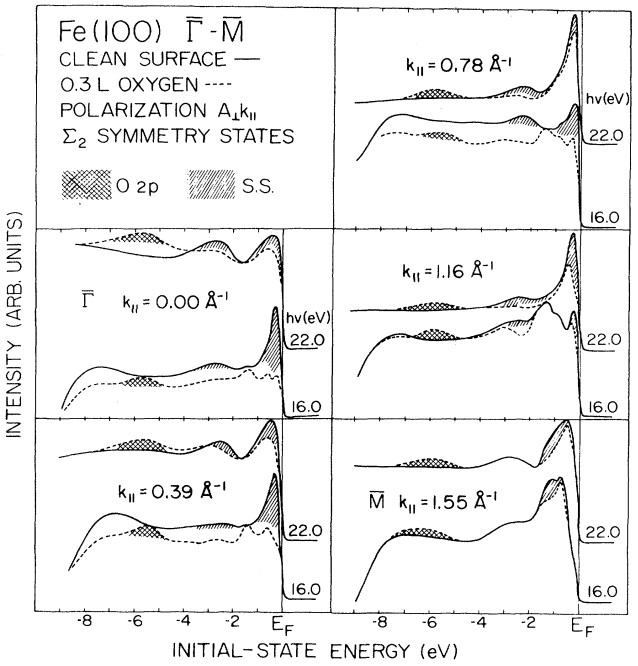

FIG. 2. Electron energy-distribution curves (EDC's) for Fe(100) surface at five values of $k_{||}$ along the $\bar{\Sigma}$ line. Dark-shaded peaks on EDC's with chemisorbed oxygen (1 L=1 langmuir=10^{-6} Torr sec) are produced by emission from oxygen $2p$ levels. Light-shaded peaks on clean EDCs identify emission from $\bar{\Sigma}_2$-symmetry surface states.

bands. A Shockley-type surface state lies in this gap for both spin bands. The same exchange-split surface-state bands are predicted by the *ab initio* (seven-layer) calculation as one can see from Fig. 1(b). The majority-spin surface-state band is filled (lies below E_F), whereas the corresponding (exchange-split) minority-spin band is only partially filled. Therefore, these odd-symmetry $\bar{\Sigma}$ bands account for part of the local surface magnetic moment on the Fe(100) surface, and it is these bands which we have identified in the experiments reported in this paper. We note here that the exchange splitting determined from photoemission spectroscopy cannot be regarded alone as an indication of the existence of spontaneous magnetization.[19]

Figure 2 displays angle-resolved-photoemission spectra for Fe(100) taken at five values of $k_{||}$ along the $\bar{\Sigma}$ line in the two-dimensional Brillouin zone. The position along $\bar{\Sigma}$ is determined by

$$k_{||}=(2mE_k/\hbar^2)^{1/2}\sin\theta\ ,$$

where E_k is the kinetic energy of electrons detected in the (010) plane along a direction determined by an angle θ measured from the normal direction [100]. The two photon energies $h\nu=16$ and 22 eV were chosen based on our extensive studies of bulk electronic properties,[17] to reduce the problems involved in identifying surface-state features in the spectra. Two spectra are presented for each photon energy and value of $k_{||}$, one for a clean surface (contamination less than 0.01 monolayer) and one for a surface having approximately 0.3 monolayer of oxygen adsorbed. Dark-shaded regions identify the oxygen $2p$ emission feature in spectra with adsorbed oxygen. Lightly shaded structures of the clean spectra originate from the exchange-split surface states. For all of the spectra shown in Fig. 2, the $\vec{A}$ vector of the linearly polarized incident radiation was perpendicular to the emission plane (defined by $k_{||}$), and therefore only odd-symmetry ($\bar{\Sigma}_2$) initial states were probed by this particular experiment.

Three criteria must be satisfied in order to correctly assign a structure in angle-resolved-photoemission spectra to a surface state: (1) The structure must be sensitive to the surface crystal perfection and surface contamination, (2) the structure must exhibit only two-dimensional dispersion, i.e., its binding can change with $k_{||}$ but not with $k_\perp$, and (3) the structure must be in a gap of the projected bulk bands of appropriate spin and spatial symmetry. In addition, it is generally helpful to have evidence from a surface calculation that the experimentally observed surface state should exist. Figure 2 shows directly that small doses of oxygen have a significant influence on the two structures in the clean-surface spectra which have been identified as originating from surface states and that the binding energies of the structures do not change with photon energy ($k_\perp$). The surface-state peaks do exhibit measurable dispersion as a function of $k_{||}$.

To check that the peaks we have assigned to surface

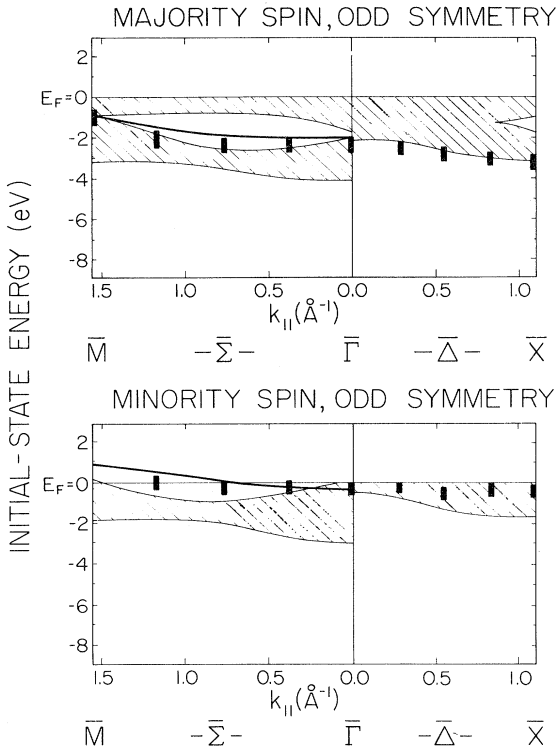

FIG. 3. Shaded regions represent bulk bands of the designated spin projected onto the two-dimensional Brillouin zone (see text). Bars at five locations along $\bar{\Delta}$ and $\bar{\Sigma}$ directions represent surface-state binding energies obtained from experimental data in Fig. 2 (experimental data for $\bar{\Delta}$ direction not shown). Heavy lines show $\bar{\Sigma}_2$ surface states predicted by the self-consistent calculation (Ref. 4).

states satisfy the third criterion, we have used a computer code[20] to calculate bulk bands along lines in the three-dimensional Brillouin zone corresponding to points along the $\bar{\Sigma}$ and $\bar{\Delta}$ lines of the two-dimensional Brillouin zone. Minor adjustments in the calculated energies were made based on the critical-point binding energies we have established using photoemission.[17] The projected bands and points corresponding to the two surface-state bands are shown in Fig. 3 along with the calculated surface-state bands (heavy lines).

The majority- and minority-spin surface-state bands exist as true surface states along most of the $\bar{\Sigma}$ line as predicted by the calculations. Along the $\bar{\Delta}$ line, it appears that both of these surface states became resonances at $\bar{\Gamma}$ where they are degenerate with bulk states. We have been able to follow the majority- and minority-spin surface bands from $\bar{\Gamma}$ along the $\bar{\Delta}$ line, and find that these bands extend to $\bar{X}$ as resonances. This behavior does not appear to have been predicted by the calculations. The exchange splitting of the $\bar{\Sigma}_2$ surface-state bands averaged over the $\bar{\Sigma}$ line is approximately 2.3 eV.

In summary, we have presented new experimental results which constitute a crucial and direct test of calculational procedures currently being used to study surface electronic properties of magnetic metals and magnetic thin-film structures. The existence of local spin polarization at the surface is confirmed by the exchange-split surface bands, and the measured splitting (2.3 eV) provides an experimental value for the surface Coloumb integral. The self-consistent surface exchange splitting at $k_{||}=0.78$ Å^{-1} is 2.4 eV, in excellent agreement with our experimental value. The corresponding parametrized calculation value (1.8 eV) is significantly lower. The calculated bulk exchange splitting[21,22] varies from 1.3 eV near the bottom of the band to 2.2 eV near the top, and our experiments[7] support these predictions. Our experimental results suggest that additional calculations for the $\bar{\Delta}$ direction could extend the tests of calculational techniques. The self-energy correction which is believed to account for the reduced exchange splitting and bandwidth in nickel does not appear to play a significant role in iron.

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[1]D. G. Dempsey, L. Kleinman, and E. Caruthers, Phys. Rev. B 12, 2932 (1975); 13, 1489 (1976); 14, 279 (1976).
[2]D. G. Dempsey and L. Kleinman, Phys. Rev. Lett. 39, 1397 (1977); D. G. Dempsey, W. Grise, and L. Kleinman, Phys. Rev. B 18, 1270 (1978); B 18, 1550 (1978).
[3]C. S. Wang and A. J. Freeman, Phys. Rev. B 21, 4585 (1980).
[4]C. S. Wang and A. J. Freeman, Phys. Rev. B 24, 4364 (1981).
[5]F. J. Arlinghaus, J. G. Gay, and J. R. Smith, Phys. Rev. B 21, 2055, (1980); 21, 2201 (1980); Phys. Rev. Lett. 42, 332 (1979).
[6]O. Jepsen, J. Madsen, and O. K. Anderson, Phys. Rev. B 26, 2790 (1982).
[7]G. Allan, Surf. Sci. Rep. 1, 121 (1981).
[8]W. Eberhardt and E. W. Plummer, Phys. Rev. B 21, 3245 (1980).
[9]F. J. Himpsel, J. A. Knapp, and D. E. Eastman, Phys. Rev. B 19, 2919 (1979).
[10]A. M. Turner and J. L. Erskine, Phys. Rev. B 25, 1983 (1982), and references cited therein.
[11]E. W. Plummer and W. Eberhardt, Phys. Rev. B 20, 1444 (1979).
[12]W. Eberhardt, E. W. Plummer, K. Horn, and J. Erskine, Phys. Rev. Lett. 45, 273 (1980).
[13]J. L. Erskine, Phys. Rev. Lett. 45, 1446 (1980).
[14]F. J. Himpsel and D. E. Eastman, Phys. Rev. Lett. 41, 507 (1978).
[15]A. M. Turner, Yu-Jeng Chang, and J. L. Erskine, Phys. Rev.

Lett. 48, 348 (1982).
[16]R. Miranda, F. Yudurain, D. Chandesris, J. Lecante, and Y. Petroff, Phys. Rev. B 25, 527 (1982).
[17]A. M. Turner, A. W. Donoho, and J. L. Erskine (unpublished).
[18]A. M. Turner and J. L. Erskine (unpublished).
[19]U. Gradmann, Phys. Rev. B 27, 1935 (1983).
[20]K. S. Sohn (private communication).
[21]J. Callaway and C. S. Wang, Phys. Rev. B 16, 2095 (1977).
[22]V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).