Spin-Resolved Photoemission of Surface States of W(110)-(1 × 1)H

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(Received 22 July 2002; published 1 November 2002)

The surface electronic states of W(110)-(1 × 1)H have been measured using spin- and angle-resolved photoemission. We directly demonstrate that the surface bands are both split and spin-polarized by the spin-orbit interaction in association with the loss of inversion symmetry near a surface. We observe 100% spin polarization of the surface states, with the spins aligned in the plane of the surface and oriented in a circular fashion relative to the $\overline{S}$ symmetry point. In contrast, no measurable polarization of nearby bulk states is observed.

DOI: 10.1103/PhysRevLett.89.216802 PACS numbers: 73.20.At, 75.70.–i, 79.60.Bm

In 1954, Néel introduced the concept of surface magnetic anisotropy and predicted that it might lead to unusual magnetic structures [1]. Since that time, the impact of the reduced symmetry at surfaces [2–4], interfaces [5], and thin films [6] on interfacial magnetic moments has been of major interest. For example, variation in the magnetic anisotropy or exchange coupling is observed as foreign atoms are adsorbed onto clean $3d$ magnetic surfaces [7–9], thereby allowing surface and thin film magnetic properties to be tailored. It is known that such phenomena result from the spin-orbit coupling between orbital and spin moments near the surface [6,10]. Despite this fundamental understanding, it came as a surprise when LaShell *et al.* [11] observed a splitting of a well-known surface state on Au(111) that they interpreted as arising from the spin-orbit interaction in association with the loss of inversion symmetry near a surface. Moreover, they predicted that the surface supports an unusual magnetic structure wherein the Bloch states are spin polarized, with spin direction in the plane of the surface and perpendicular to the Bloch wave vector. This hypothesis has lead to some dispute since the splitting was not observed in previous photoemission experiments or in STM measurements. While more recent photoemission and theoretical results on Au(111) [12,13] and a similar photoemission study of Mo(110) and W(110) surfaces [14,15] support the original hypothesis, the key prediction — spin polarized surface states on a nominally nonmagnetic surface — remains unconfirmed.

In this paper, we directly validate the hypothesized spin polarization of surface bands. We have performed spin- and angle-resolved photoemission experiments to measure the surface electronic states on W(110)-(1 × 1)H. We find that the relevant surface states are indeed 100% spin polarized in precisely the way predicted [14]. This observation confirms the proposal that the spin structure plays a key role in coupling electron-hole pairs to phonon excitations on this surface [15]. Moreover, the unusual k-space spin structure will have a significant impact on interfacial magnetic structures. Although it may be difficult to resolve the splitting in $3d$ and $4d$ systems in which the spin-orbit interaction is reduced [12], it may nonetheless have a strong impact on magnetic structure.

The spin-orbit interaction generally lowers the symmetry of the electronic Hamiltonian and therefore splits one-electron energy levels in atoms, molecules, and solids [16,17]. This splitting is caused by a relativistic correction to the Schrödinger equation, which to lowest order is given by

$$\mathcal{H}_{\mathrm{SO}} \propto \vec{\sigma} \cdot \vec{B}_{\mathrm{ind}} = \frac{\hbar}{4m^2c^2} \vec{\sigma} \cdot (\vec{\nabla} V \times \vec{p}), \qquad (1)$$

where $\vec{\nabla} V$ is the external potential energy, $\vec{p}$ is the electron momentum, and $\vec{\sigma}$ is the Pauli spin operator. The electron experiences a magnetic field in its rest frame that arises from the Lorentz transformation of the static external electric field, $\vec{E} = \vec{\nabla} V$. Zeeman splitting then lifts the degeneracy of various spin-degenerate levels. This splitting, however, is forbidden in centrosymmetric solids due to the combined influence of time reversal and inversion symmetry [17,18]. The absence of an inversion center at the crystal surface breaks this symmetry, and in principle allows bands to split into subbands of opposite spin in the vicinity of the surface. This is the mechanism proposed by LaShell *et al.* [11]. In this case, $\vec{\nabla} V$ pertains to the surface potential energy gradient, though the magnitude of the observed splitting also depends on the atomic spin-orbit parameter [12,13]. The effect is most pronounced in heavy metals for this reason; much smaller

splittings were observed on closely related Ag(111) [12] and Mo(110) [14] surfaces.

A W(110) crystal was cleaned with techniques described elsewhere [19]. Hydrogen coverage was calibrated according to the W $4f$ surface core-level shifts [20]. Angle-resolved and spin- and angle-resolved photoemission experiments were performed *in situ* near 130 K using undulator-generated soft x-rays at beamline 7 of the Advanced Light Source [21]. The angular resolution for non-spin-resolved photoemision was better than 0.75°, while the total instrumental energy resolution was ~100 meV. Spin-resolved photoemission was performed with a mini-Mott detector at an energy of 24 keV [22]. The Sherman function for the Mott detector is $S = 0.12$. The angular resolution for spin-polarized photoemission was better than 2°, while the instrumental energy resolution was ~300 meV. Our apparatus allows measurement of the spin-polarization components (a) in the sample surface plane but perpendicular to the plane containing the surface normal and the photoelectron momentum ($\sigma_{z\pm}$), and (b) parallel to the photoelectron momentum ($\sigma_{x\pm}$). In conventional magnetic materials, to normalize any instrumental asymmetry, the spin polarization is determined by switching an applied magnetic field and combining the measured intensities I_R and I_L. Because our system has no net magnetic moment, no external field needs to be applied. We determined the instrumental asymmetry A at a k point where the surface states are absent. The spin polarization can then be written as $p = (1/S)(I_L - AI_R)/(I_L + AI_R)$ and the individual spin-up and spin-down spectra as $\sigma_\pm = (I_L + I_R)(1 \pm p)/2$.

Figure 1(a) shows the photoemission intensity at the Fermi energy (E_F) for W(110)-(1 × 1)H as a function of parallel momentum through parts of the first and second surface Brillouin zones (SBZs). Bright regions correspond to places where surface or bulk bands cross E_F. The former are highlighted with lines as guides to the eye and are labeled with numbers in accord with previous publications [15]. Figure 1(b) shows the corresponding valence band map (binding energy vs momentum) along the $\overline{\Gamma} \rightarrow \overline{S}$ direction. In both panels, the features near the center of the SBZ arise from transitions from bulk states. Details concerning the evolution of the surface states and their relation to surface phonon anomalies can be found elsewhere [14,15].

The filled and empty triangles in Fig. 2 show the spin-up and spin-down photoemission intensities, respectively, at the point labeled D in Fig. 1 over most of the occupied W d band. The in-plane spin component ($\sigma_{z\pm}$) and the spin component parallel to the photoelectron momentum ($\sigma_{x\pm}$) are shown in the left and right panels, respectively. Also shown are the respective spin polarizations as a function of binding energy.

The left panel reflects the degree of in-plane spin polarization tangential to the Fermi contours of bands S_1 and S_2 where they intersect the $\overline{\Gamma} \rightarrow \overline{S}$ line. While 100% spin polarization is evident in the surface states S_1 and S_2, no spin polarization at all is observed in the bulk states, within our statistics. The right panel probes a combination of the out-of-plane spin component and the in-plane spin component parallel to the initial state parallel momentum. We observe no measurable surface or bulk state spin components in these directions, verifying the predicted 100% in-plane spin polarization tangential to the Fermi contour [11–13].

Further evidence for the validity of LaShell's hypothesis comes from measuring how the spin polarization varies at different points on the contour. Figure 3 shows spin-resolved spectra of the surface states only for the in-plane tangential components ($\sigma_{z\pm}$) and polarization P at the points A, B, C, and D denoted in Fig. 1. The arrows in Fig. 1(a) indicate the measured orientation of the spin

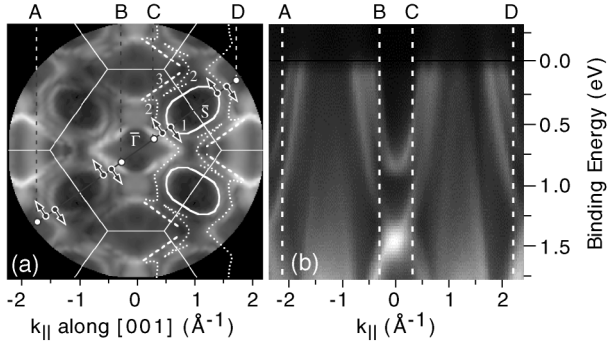

FIG. 1. (a) Photoemission intensity at E_F for W(110)-(1 × 1)H in the first and parts of the second surface Brillouin zone. Surface orbits are indicated with lines as guides to the eye. The points A, B, C, and D indicate the positions where we report spin-polarized photoemission results, and arrows represent the spin directions deduced from spin-resolved measurements. (b) Corresponding valence band map along the $\overline{\Gamma} \rightarrow \overline{S}$ direction.

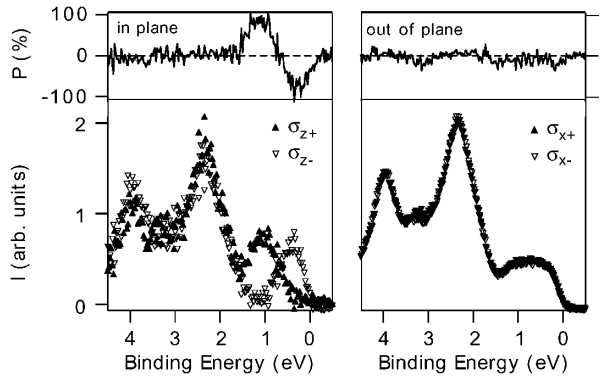

FIG. 2. Spin-resolved photoemission intensities over most of the occupied tungsten d band measured at point D in Fig. 1. The tangential, in-plane spin components ($\sigma_{z\pm}$) and the spin components measured along the photoelectron momentum vector ($\sigma_{x\pm}$) are reported in the right and left panels, respectively, as well as the resulting spin polarizations.

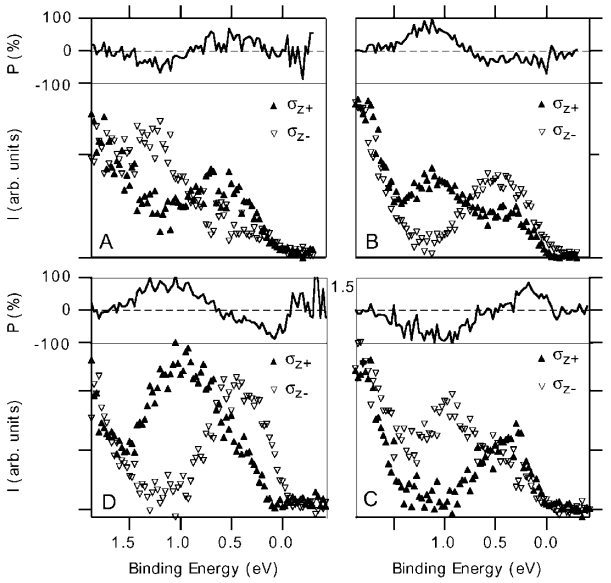

FIG. 3. Spin-resolved photoemission intensities for the surface states in the in-plane, tangential components ($\sigma_{z\pm}$) and polarization P at the positions A, B, C, and D.

direction for states near these points on the associated Fermi contours. As required by the Kramers degeneracy [16,17], $E(k_{\parallel,\uparrow}) = E(-k_{\parallel,\downarrow})$, we observe reversal of the spin polarization for equivalent surface states on opposite sides of zone center.

An interesting aspect of these results is that the spin direction is reversed for states on opposite sides of $\overline{\mathrm{S}}$ symmetry point. Evidently the spin direction circulates around the $\overline{\mathrm{S}}$ point roughly tangentially to the Fermi contours. If on the other hand the relevant momentum were measured relative to $k_{\parallel} = 0$, then Eq. (1) would not predict reversal of the spin direction between points A and B, for example, which lie on the same side of $k_{\parallel} = 0$. Indeed, the combination of reciprocal lattice symmetry, $E(k_{\parallel} + g_{\parallel}) = E(-k_{\parallel})$, with Kramers degeneracy *requires* that reversal of the spin direction be observed across $\overline{\mathrm{S}}$. This observation suggests that the canonical momentum in Eq. (1) should be replaced with the effective mass times the Bloch velocity of the surface bands. This makes sense because the quasiparticles travel at the Bloch velocity, which is therefore the relevant velocity in the Lorentz transformation of the electric field associated with the surface barrier. The Bloch velocity reverses for states on the opposite side of $\overline{\mathrm{S}}$, so that the spin direction naturally will be inverted. Indeed, for an electron, $\vec{\nabla} V$ is directed parallel to the surface normal, and Eq. (1) accurately predicts the sense of the observed spin directions labeled with arrows in Fig. 1. Applying a similar analysis to other mirror and inversion symmetry-related S_1 contours, we find that the spin direction will always be tangential to the Fermi contour while orbiting the $\overline{\mathrm{S}}$ points in a counterclockwise fashion.

LaShell observed that spin-orbit split bands are effectively shifted in k space so that the band origins lie on opposite sides of the relevant symmetry point [11]. The bands that give rise to contours S_1 and S_2 are clearly visible in Fig. 1(b). In contrast to LaShell's observations on Au(111), these two bands appear to be individually symmetric about both $\overline{\Gamma}$ and $\overline{\mathrm{S}}$ and also to be split at $\overline{\Gamma}$. Our results exhibit these qualitative differences from LaShell's results because these surface bands disperse through a bulk continuum located near $\overline{\Gamma}$ where they lose their surface character, as shown in the left panel of Fig. 4.

Indeed, near zone center, the bands are degenerate with the spin-orbit split (but not spin-polarized) components of the bulk $\Gamma_{25'}$ level. In the right panel of Fig. 4, we show the magnitude of the tangential spin polarization of the two surface bands S_1 and S_2 as a function of parallel momentum near the center of the SBZ. The bands lose their spin polarization as they disperse through the bulk continuum. This result is precisely counter to early observations of induced spin polarization of adsorbate bands degenerate with a bulk continuum on a magnetic substrate [23]. The fact that the spin polarization appears to decrease monotonically as the bulk continuum is approached very likely results from the limited momentum resolution of the spin-resolving apparatus; the underlying transition may be more abrupt than indicated. First-principles, fully relativistic calculations of these surface bands will help unravel the interesting issue of how the surface state spin polarization is quenched as the band approaches the bulk continuum.

Finally, we compare our results to other systems where spin-polarized photocurrents have been observed. These can be categorized as systems with spin polarization endemic to the initial state, systems that produce spin polarization in the excitation process, and systems that produce spin polarization by final state scattering [24]. Spin is an axial vector and it must be defined relative to another reference axial vector. In the present case, the polarization exists in the initial state and the requisite axial vector is evidently $\vec{\nabla} V \times \vec{p}$, from Eq. (1). The

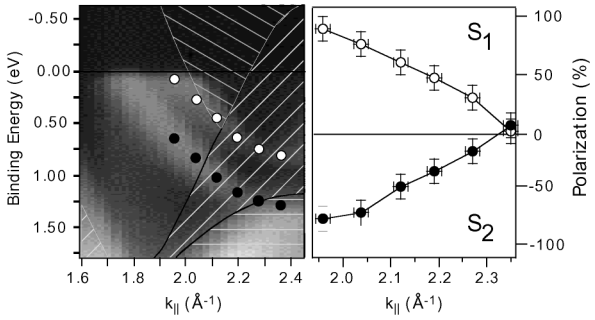

FIG. 4. Left panel: Measured dispersion relations for the two surface bands S_1 and S_2, superposed on the hatched projection of the bulk band structure. Right panel: Measured tangential spin polarization of the two surface bands S_1 and S_2 as a function of parallel momentum near the center of the surface Brillouin zone. Lines are guides to the eye.

orientation of this vector depends on the crystal momentum of the state being probed, so that the orientation of the spin polarization naturally varies with $\vec{k}$. The orientation depends also on $\vec{\nabla}V$, which is fixed macroscopically since it is normal to the surface plane. These observations explain qualitatively why we observe 100% spin-polarized photocurrents from surface bands on this nonmagnetic surface.

The effect we have documented is related to several previous experiments, but is different in detail. In ferromagnetic systems, for example, the polarization exists in the initial state but the reference axial vector is the magnetization $\vec{M}$ [25]. The spin-orbit interaction determines magnetization anisotropy, but the magnetization itself is produced by exchange. Initial state-spin polarization has also been observed in photoemission from bulk GaAs bands at $k \neq 0$ that are spin-split by the spin-orbit interaction. The reference axial vector is $\vec{\nabla}V \times \vec{p}$, as in the present case, but $\vec{\nabla}V$ is related to the inherent lack of inversion symmetry of the bulk lattice rather than the surface potential. Negative electron affinity GaAs spin-polarized photocathodes offer a well-known example of a system where the polarization is produced by zone-center dipole transitions between spin-orbit split bulk bands. The reference axial vector is the photon angular momentum vector [26]. Related phenomena have been observed in valence band photoemission from Pt(111) [27] and in photoemission from spin-orbit split core levels using linear polarization [28]. Spin polarization produced by final state scattering was first observed on W(100) [24] and is closely related to the mechanism involved in a LEED-type spin detector [29]. The spin polarization results from the combined influence of the surface barrier and the spin-orbit interaction. The underlying interaction is therefore very similar to the present case, though there are no spin-split bound states and the relation to surface magnetic anisotropy is indirect. Finally, spin-dependent photoemission intensities from bulk bands on Pt(111) were interpreted in terms of the spin-orbit interaction and the lack of inversion symmetry [30,31]. However, there was no spin-splitting in the initial state.

In conclusion, we observed 100% in-plane spin polarization of the surface states of W(110)-(1×1)H, as proposed to be due to spin-orbit interaction. The measurements show the reversal of the polarization across the zone boundary at $\overline{S}$ and that the spin-direction orbits the $\overline{S}$ points in a counterclockwise direction, in accord with the predictions based on the spin-orbit Hamiltonian. Clearly, the effect we observed in a nonmagnetic system will complicate the interpretation of spin-resolved spectra in magnetic systems as well. Related effects may have a pronounced impact on surface and interface magnetic anisotropy in this and other systems.

This work was supported by the U.S. Department of Energy under Grants No. DE-FG06-86ER45275 and No. W-7405-Eng-48. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. DOE under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory.

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