

Spin-Orbit Coupling Induced Surface Band Splitting in Li/W(110) and Li/Mo(110)

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The broken symmetry at surfaces can give rise to a nonzero spin-orbit splitting of valence bands. We observe such a splitting of the d -derived surface state on W(110) and, to a lesser extent, on Mo(110), and follow the evolution of the splitting as monovalent atoms are adsorbed. The observed evolution is directly relevant to recent observations of altered orbital magnetic structure versus adsorbate coverage in magnetic materials. We propose a spin ordering for the associated Fermi contours which has important implications for spin excitations at surfaces. [S0031-9007(99)09192-9]

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The change in magnetic moment induced by the reduced symmetry at surfaces [1–3], interfaces [4], thin films [5], and step edges [6] has been a subject of intense study recently due to its technological implications. One fascinating aspect is the variation in magnetic structure, such as anisotropy or exchange coupling, as small amounts of foreign atoms are adsorbed onto clean magnetic surfaces [6–8]. While it is known that these phenomena result from a subtle interplay between orbital and spin moments through the spin-orbit coupling (SOC) interaction $H_{\text{SOC}} \sim \xi \mathbf{L} \cdot \mathbf{S}$ [5,9], accurate theoretical predictions of magnetic structure remain difficult [10]. Experimental elucidation of the spin-orbit coupling as a function of adsorbate coverage, which might be manifested in surface band structure measurements, is therefore of great interest. However, for the relevant $3d$ transition metals (Co, Fe, etc.), direct observation of valence band electronic states versus coverage is difficult due to the large linewidths and the small energy splittings involved.

An alternate approach is to consider some *non-magnetic*, heavy transition metals where the spin-orbit effects are enhanced. In these cases the coupling H_{SOC} induces a spin-orbit splitting of the surface states, for example, in the sp -derived surface state at $\bar{\Gamma}$ on Au(111) [11]. Here, the spin-orbit splitting, attributed to a change in the orbital moment $\langle L_z \rangle$, is observable because the Au d bands are well separated from the Fermi level where the spin-orbit splitting in the surface sp band is strongest.

In this paper, we show that a similar, though substantially larger, spin-orbit splitting exists in d -derived surface bands on W(110) and, to a lesser extent, to Mo(110). These d -derived band splittings are comparable to typical exchange splittings in ferro- and antiferromagnets. More importantly, we show that the magnitude of the splitting can be modified by very low coverages of monovalent atoms, similar to the extreme sensitivity of magnetic

anisotropy to adsorbate coverage. In contrast to magnetic measurements, where changes of ΔH_{SOC} with adsorbate coverage contribute only indirectly to the observed changes in magnetic structure, here ΔH_{SOC} contributes directly to the observed energy shifts of the surface bands in a manner which can be measured continuously versus adsorbate coverage.

The change in spin-orbit coupling affects not only the ground state properties but also the dynamical properties such as the electron-phonon coupling. This comes about because of the associated change in the topology of the Fermi contours as a function of coverage. Since these contours are expected to exhibit interesting spin orderings, our results suggest an unusually complex coverage-dependent spectrum of spin excitations on these surfaces.

Lithium was deposited from SAES getters held ~ 1 cm from the cleaned [12] sample surfaces. We consider 1 monolayer (ML) coverage to be achieved when a second layer of Li begins to form, indicated by the presence of a surface core level shift in the Li $1s$ core level. Similar to Li on other metals [13], we estimate that at this coverage only about 85% of the surface W or Mo atoms will be fully coordinated with Li. Angle-resolved photoemission (ARP) measurements were performed *in situ* at beam line 7.0 of the Advanced Light Source [14] with photon energy 100.00 eV; other experimental details are described elsewhere [15]. Analysis of surface core level shifts (Mo $3d$, W $4f$, Li $1s$) implies uniform, 2-dimensional growth, and rules out reconstructions, clustering, etc., consistent with growth on many other close-packed surfaces [13].

Figure 1(a) shows clean W(110) valence band spectra as a function of polar angle $15^\circ < \theta < 35^\circ$, from the boundary of the first surface Brillouin zone (SBZ) (\bar{S}) to the center of the second SBZ ($\bar{\Gamma}_1$). The most important feature is the pair of states, assigned as surface states

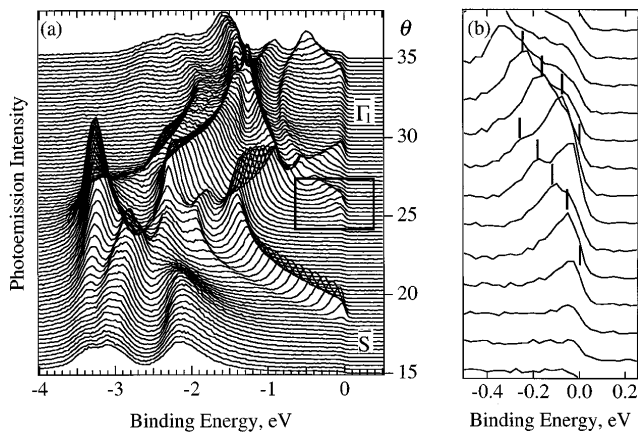


FIG. 1. Angle-resolved valence band photoemission for the clean W(110) surface. (a) Series of individual spectra vs polar angle θ ; (b) same as the rectangular region in (a).

using standard criteria [15,16], which cross the Fermi level E_F at $\theta \sim 26^\circ$, as shown more clearly in Fig. 1(b). We believe that these states originate from a single band that has been split by the spin-orbit interaction. While the original state is well known theoretically and experimentally [12,17–19], the fact that there is a splitting is new to this study. We will show that the binding energies of these states, and hence their Fermi wave vectors k_F , are very sensitive to the presence of adsorbates.

Figure 2(a) shows the surface bands versus parallel momentum k_{\parallel} derived from Fig. 1(a), together with the interpolated bulk tungsten band structure projected onto the (110) surface [20]. The two surface bands discussed

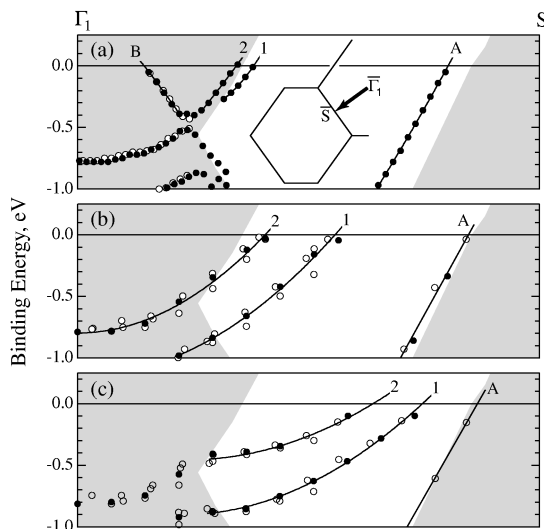


FIG. 2. Angle-resolved surface valence bands for Li on W(110) vs Li coverage. (a) Clean W(110); (b) ~ 0.5 ML Li; (c) 1.0 ML Li. The shaded region is the projection of bulk states onto the (110) surface. The closed circles are for momenta as indicated in the inset; open circles are from other symmetry-equivalent directions.

previously, now labeled 1 and 2, lie close to the top edge of a large projected gap in bulk states. State 1 lies well within the projected gap of bulk states, and may be properly labeled a surface state. State 2, on the other hand, lies very close to the projection of bulk states and hence might be labeled a surface resonance on the clean surface [16]. Two other sharp and distinct bands, labeled A and B, exhibit Fermi level crossings as well.

Figures 2(b,c) show the effect of lithium adsorption on the various bands. As Li accumulates, bands 1 and 2 shift down in energy; meanwhile, the energy splitting between these two bands widens dramatically, from <0.2 eV on the clean surface [Fig. 2(a)] to about 0.5 eV at 0.5 ML Li coverage. At higher coverages, while bands 1 and 2 continue to move down in energy, their relative energy splitting decreases slightly to ~ 0.4 eV. Seven coverages were examined, which demonstrate that the changes in Figs. 2(a–c) evolve smoothly and uniformly with coverage. There is an obvious kink in the bands at higher coverage as they cross from the gap into the bulk states near $\bar{\Gamma}$, a possible manifestation of the surface state \rightarrow resonance transition [21]. Bands A and B are also shifted down in energy (with band B broadening considerably and no longer crossing E_F), and they continue to show no splitting. While we focus here on lithium adsorption, qualitatively similar results are observed upon adsorption of all the alkali metals [22] as well as hydrogen [15].

We now turn to Fig. 3, which shows similar data for lithium adsorption onto Mo(110). Figure 3(a) shows band mapping results for the clean Mo(110) surface within the first SBZ. We see a clear correspondence between each band in Figs. 3(a) and 2(a), with the Mo bands located ~ 0.5 eV closer to E_F than the W bands. The only difference (apparently minor for the clean surface) is that whereas for W we barely distinguish two states 1 and 2, for Mo we see a single state, which we label 1 + 2 here. For W, we saw a clear trend to increase the splitting between 1 and 2 (up to ~ 0.5 eV) upon Li adsorption. Figure 3(b) shows that a similar, smaller

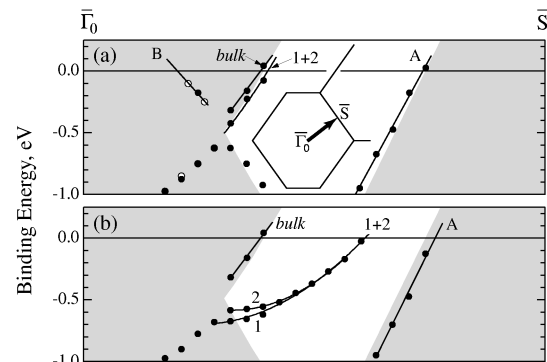


FIG. 3. Angle-resolved valence bands for Li on Mo(110) vs Li coverage. (a) Clean; (b) 1.0 ML Li. The closed circles are for momenta as indicated in the inset; open circles are from other symmetry-equivalent directions.

splitting (~ 0.13 eV) develops in band 1 + 2 upon Li exposure at binding energy ~ 0.6 eV. (While there is a weaker, unrelated bulk feature near 1 + 2 for the clean surface, our conclusions remain unchanged when we examined equivalent surface bands in another SBZ where the bulk transition is absent.) Preliminary data for clean, epitaxial Cr(110) films, deposited on either the same W(110) or Mo(110) crystals used here, also show a single 1 + 2 state as in Mo(110) [23].

Similar to the case of Au(111) [11], we propose the splitting between bands 1 and 2 to be due to the spin-orbit interaction, given by the Hamiltonian

$$H_{\text{SOC}} = (\hbar^2/4m^2c^2)(\vec{\nabla}V \times \vec{p}) \cdot \vec{\sigma} \approx \xi \mathbf{L} \cdot \mathbf{S}. \quad (1)$$

The high nuclear mass of W (and consequently larger p) compared to Mo makes this relativistic effect much more important for W. The magnitude of the band splitting, while difficult to predict quantitatively, ought to be comparable to the spin-orbit parameters. These are 0.12 eV and 0.45 eV for the Mo $4d$ and W $5d$ levels, respectively [24], in surprisingly good accord with our results at full Li coverage. The variation in $\vec{\nabla}V$ with coverage then reflects the alteration of the surface with adsorption. No other possible effect, e.g., surface reconstruction, adsorbate ordering, etc., provides a plausible explanation of the systematic evolution of the splitting as a function of coverage for all monovalent atoms.

Why does the splitting evolve with Li coverage? Since the splitting vanishes in the presence of inversion symmetry, and both W and Mo are centrosymmetric in the bulk, the surface itself is required for the proposed splitting to occur [25]. Remarkably, the changes to the W/Mo surface environment by Li adsorption are even more dramatic than the initial creation of the vacuum interface; otherwise we might expect the splitting to decrease with Li coverage instead of increase. We emphasize that the splitting behaves in a qualitatively similar fashion for hydrogen and all other alkali metal adsorbates, independent of size or mass. This unified evolution of the splitting can be largely explained by the extreme change in localization of states 1 and 2 with coverage: more bulklike at low coverage where they are very close to the bulk continuum to more surface localized at high coverages where they lie deep in the bulk band gap. The adsorption-induced change in magnitude of the potential gradient in Eq. (1) and the extent to which this gradient is sampled by the surface state wave function conspire to determine the magnitude of the splitting. In contrast, states *A* and *B* in Fig. 2 are not split, consistent with their poor surface localization (they are close to or within, and hence resonant with, the bulk continuum). Similarly, unlike states 1 and 2, states *A* and *B* do not drive surface phonon anomalies [26,27].

Surface localization cannot provide the entire explanation of our results, however, since the energy splitting is

not a monotonic function of depth in the gap (in fact, appearing largest near the edge of the projected bulk states at the highest coverages). Indeed, the behavior of this splitting with coverage is very similar to that of the work function change, suggesting that variation of the surface potential gradient plays a significant role as well. The observed spin-orbit splitting might thus provide a useful local probe of surface potential gradients, showing more than an order of magnitude larger change as compared to the traditionally studied surface core level shifts [28].

These results are relevant to the altered magnetic structure at surfaces, interfaces, and step edges. The spin-orbit splitting we measure is a sensitive function of surface localization, electrostatic potential, and hybridization, indicating a changing orbital moment with adsorbate coverage, which indeed shows the same sensitivities [2]. In magnetic systems, this change in orbital moment is believed to be largely responsible for altered magnetic anisotropy. However, where anisotropy energies turn out to be small (~ 1 meV) and difficult to calculate, the alteration in spin-orbit splitting is large and easy to measure. Furthermore, additional information on the effects of charge rearrangement, due to both interaction with the alkali s -levels as well as screening charge rearrangement (in response to the altered surface potential) could also be inferred from our data, and may be a factor in the magnetic systems as well.

Having established that spin-orbit coupling is responsible for the splitting between bands 1 and 2, we now consider the spin ordering of these states. Since $\vec{\nabla}V$ is out of the surface plane and \vec{p} is in the plane, the energy splitting must be primarily between in-plane polarized spins. In the simple case of the sp -derived surface state on Au(111), which is close to and circularly symmetric about zone center, the net energy shift turned out to be proportional to k_{\parallel} [11]. In our situation, the surface states are d derived and are far from zone center and close to bulk band edges. The resulting complex morphology of the energy surfaces will cause a more complicated functional dependence of the spin ordering on k_{\parallel} . While we lack a detailed theory, we are nonetheless motivated to develop a simple picture of the spin ordering.

Figure 4 shows the valence band ARP intensity at the Fermi level for 1 ML of Li on W(110) [Fig. 4(a)] and on Mo(110) [Fig. 4(b)] in and beyond the first SBZ. The data were taken over a 90° sector and symmetrized to get the 180° images shown, although we carefully checked that the symmetry was in fact properly obeyed. The collection of Fermi-level crossings by bands 1 and 2 form Fermi contours as shown, which are hole orbits. The arrows show the proposed relative in-plane spin orientations. The arrows have the property that states across mirror planes have their spin component parallel to the mirror plane flipped, as required by time-reversal symmetry. Clearly, the case of Li on Mo(110) in Fig. 4(b) has a Fermi contour that is insignificantly split compared to that of Li on W(110). Although there are other nearby crossings

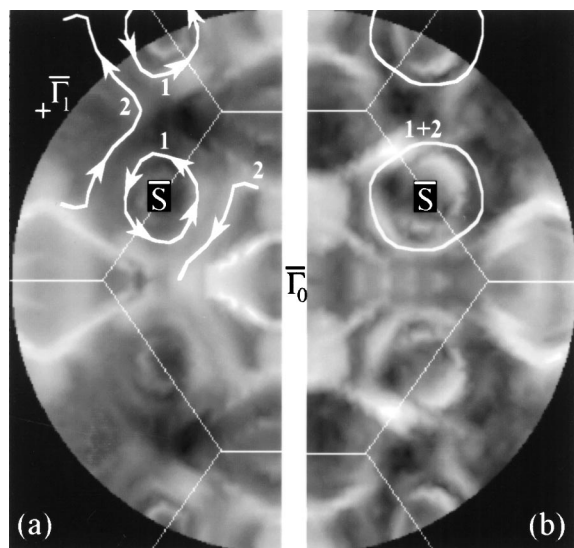


FIG. 4. Fermi intensity maps for 1 ML of Li deposited on (a) W(110) and (b) Mo(110). The straight white lines are the surface Brillouin zone boundaries; the remaining white lines in the upper part denote the Fermi crossings, derived from the mirror-reflected raw data (lower part).

apparent in the image, these are all assigned to unrelated bulk or surface states and, in any case, are also present for W.

Why should these states and their Fermi contours be so interesting? In addition to explaining why a small adsorbate coverage can have a dramatic impact on magnetic anisotropy, the spin orderings we observed will very likely impact the interfacial magnetic structure between a heavy metal like tungsten and a magnetic metal, a topic of intense current interest. They should also have a profound effect on the elementary excitations at these surfaces. For example, there has been much recent theoretical attention to the issue of electron-phonon coupling on the closely related surfaces H on W(110) and H on Mo(110) [17,18,26,27]. A strong softening of the surface phonons is observed at particular nesting vectors, which has been attributed to Kohn anomalies. This means that phonons of specific wave vector, the location of which is determined by Fermi contours such as these, decay with high efficiency into electron-hole pair excitations. The observed spin splitting implies that spin conservation needs to be taken into consideration as part of this electron-phonon coupling process [15], which was not predicted by recent calculations [17–19]. Moreover, there will be distinct spin excitations at these surfaces, and the dispersion relations of these will be determined by the spin ordering of these contours.

In conclusion, we have observed and characterized a splitting of surface bands on W(110) and Mo(110) that is attributed to the spin-orbit-coupling interaction. When coupled to first-principles calculations, this splitting will

provide an unusual probe of the surface potential gradient. The resulting spin ordering of the Fermi contours will also impact the excitation properties of these and related surfaces.

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