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Advanced Light Source Division

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(July 1, 1998)

We observe a significant splitting of a surface band on W(110), while the analogous band on Mo(110) is split to a much smaller extent. We conclude that this splitting is due to the spin-orbit interaction, similar to that recently proposed for Au(111). A smooth evolution of the magnitude of the splitting as monovalent atoms are adsorbed is attributed to increased surface localization of the wave function and to the altered potential gradient at the interface. We propose a spin ordering of the associated Fermi contours which has important implications for the electronic and spin excitations at this and closely related surfaces.

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Under what circumstances can a material that is nonmagnetic in the bulk exhibit a magnetic structure at its surface? How does the existence of surface magnetic structure impact the structural and transport properties of a surface and the spectrum of excitations near a surface? Can we control the magnetic structure by varying, for example, the material adsorbed onto of the surface? Fundamental questions such as these continue to provide an enduring research focus while also driving important magnetic thin film technologies. An interesting and potentially important aspect of these questions was recently reported by Jensen, et al. [1]. Employing angle-resolved photoemission (ARP), they reexamined the well-known zone-center surface state on Au(111) with extremely high angular and energy resolution. They found, contrary to earlier studies [2,3], that this sp-derived surface state was split, and that the most likely source of the splitting was the spin-orbit interaction. They further concluded that the surface state exhibits an unusual spin ordering wherein the spin direction 'orbits' about the center of the surface Brillouin zone (SBZ), in an opposite direction for each split band.

In this paper, we show that a similar though substantially larger splitting exists in d-derived surface bands on W(110) and, to a lesser degree, on Mo(110). These iso-electronic surfaces have almost identical lattice constants and thus have, apart from relativistic effects, nearly identical surface and bulk electronic properties. Based on the atomic spin-orbit couplings [4], we would expect any surface state splitting to be significantly larger for tungsten than for molybdenum. Indeed, we observe a splitting as large as \( \sim 0.5 \, \text{eV} \) for W(110), but only \( \sim 0.1 \, \text{eV} \) for 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 adsorption of monovalent atoms, leading in many cases to gross changes in the topology of the associated Fermi contours. Since these contours are expected to exhibit the same sort of spin- orderings as those proposed by Jensen, et al. [1], our results suggest an unusually complex, coverage-dependent spectrum of spin excitations on these surfaces. Similarly, the splitting plays an important role in determining the location of phonon anomalies on these surfaces [5-9]. We will discuss these changes in surface band energy splitting and speculate upon the generality of our results.

We prepared the clean crystals using standard techniques [10]. Lithium was deposited from well-outgassed SAES getters held \( \sim 1 \, \text{cm} \) from the sample surface. 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 [11], we estimate that at this coverage only about 85% of the surface W or Mo atoms will be fully coordinated with Li. ARP measurements were performed in situ at beamline 7.0 of the Advanced Light Source at Lawrence Berkeley National Laboratory [12]. The hemispherical electron spectrometer’s axis and the photon polarization vector were coplanar with and kept at fixed angles (90° and 30°, respectively) to the sample’s polar rotation axis. The angular resolution was better than 0.75°, while the total instrumental energy resolution was ∼100 meV. Band maps are composed of valence band spectra (typically 30 s each) acquired while varying the polar angle θ of the sample, in 1/2° or 1/4° steps. Conversion of transitions with binding energy E at emission angle θ to k-space coordinates was through $k_{\parallel} = 0.5124(hv - E - \Phi_W)^{1/2} \sin \theta$, where E is negative, $\Phi_W$ is the work function, and $hv = 100$ eV is the photon energy for all data presented. Surface states were distinguished from bulk states by checking the independence of their binding energies with wavevector normal to the surface ($k_{\perp}$), their sensitivity to adsorbates, and whether they exist within gaps in the projection of bulk states projected onto the (110) SBZ [13].

Fig. 1 shows valence band spectra at photon energy $hv = 100.0$ eV as a function of polar angle for the clean W(110) surface. Fig. 1(a) shows spectra taken with 15° < θ < 35°, a range which roughly spans from the boundary of the first SBZ (denoted $\bar{S}$) to the center of the second SBZ (denoted $\bar{\Gamma}$). The feature of particular interest for the rest of this paper is the pair of states, assigned as surfaces states using the above criteria, which cross the Fermi level $E_F$ at θ ∼ 26°, 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 [7-10], the fact that there is a splitting is new to this study. The binding energies of these states, and hence their Fermi wave vectors $k_F$, are very sensitive to the presence of adsorbates. Visualization of the states is often easier when plotted in an image format (Figs. 2-4), where the valence band intensity is mapped from black (low intensity) to white (high intensity); henceforth we will only present such gray-scale images.

Fig. 2(a) shows such a grey scale band mapping for the data in Fig. 1(a), after converting the horizontal axis to parallel momentum $k_{\parallel}$. Only those data of less than 1 eV binding energy are now shown. We also indicate, with hatched lines, the bulk tungsten band structure projected onto the (110) surface calculated using the interpolation method of Papaconstantopoulos [14]. Although the calculation is only accurate to a few tenths of an eV, we find that it predicts the known edges of the projected bulk continua at $E_F$ to within 0.01 Å⁻¹. The two surface bands discussed previously, now labeled 1 and 2, lie close to the top edge of a large projected gap along the direction. 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 [13]. Additionally, two other bands exhibit Fermi level crossing crossings and are labeled A and B. Neither of these exhibits the splitting observed for states 1 and 2.

Figs. 2(b,c) show the effect of lithium adsorption on the various bands. Bands 1 and 2 are shifted down in energy and well into the projected band gap. Furthermore, 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 1.0 ML coverage (Fig. 2(c)), bands 1 and 2 have moved slightly further down in energy, although the energy separation of the bands decreases slightly to ∼0.4 eV. 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 → resonance transition [15]. 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, the qualitatively similar results are observed upon adsorption of hydrogen and all alkali metals [16].

We now turn to Fig. 3, which shows similar data for lithium adsorption onto Mo(110). Fig. 3(a) shows band
tungsten and molybdenum are centrosymmetric in the
bulk, the surface itself is required for the proposed split­
ing to occur. According to Eq. 1, the magnitude of the
splitting must then be related to the gradient of the sur­face potential, primarily in the vicinity of the ion cores
in the first layer. The magnitude of this potential gradient,
and the extent to which it is sampled by the surface state
wave function, conspire to determine the magnitude of the
splitting. For example, the fact that states A and B in Fig. 2 exhibit no measurable splitting must indicate
that the corresponding wave functions do not sample the
surface potential gradient very effectively. They presum­ably are not highly localized to the surface region. This
makes qualitative sense: B is resonant with bulk states,
while A is very close to the bulk continuum on the clean
surface and actually moves into the bulk continuum upon
alkali adsorption. That these states do not drive surface
localization probably does not provide the entire explana­tion of our results. Indeed, the behavior of this splitting is
very similar to that of the work function change, suggest­ing that variation of the surface potential gradient plays
a significant role as well. This observation suggests that the
observed spin-orbit splitting might provide a useful, local
probe of surface potential gradients.

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. Following Jensen,
et al. [1], we note that since \( \overline{\nabla}V \) 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 \( k_\parallel \). In

Why should the splitting evolve with Li coverage? Note
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\[
H_{SO} = \hbar^2/4m^2\vec{c}^2 (\overline{\nabla}V \times \vec{p}) \cdot \vec{\sigma}. \tag{1}
\]

The high nuclear mass of tungsten compared to molyb­denum makes relativistic effects much more important for
tungsten. The magnitude of the band splitting, while dif­
cult 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 [4], in
surprisingly good accord with our results at full Li cov­erage. Also, as discussed by Jensen et al. [1], without
using circularly polarized light and spin detection, the split
peaks should have the same integrated intensity. This
is clearly true when both states 1 and 2 are well
within the bulk gap (Fig. 2(b,c) and Fig. 3(c)). Only on
clean W(110) do the peaks differ in height, although this
is quite reasonable since band 1 (being closer to the con­
tinuum) will penetrate further into the bulk than band 2
and hence have a different transition probability and less
weight in the surface layers probed by photoemission. 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.

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![FIG. 3. Angle-resolved valence band photoemission for Li on Mo(110) vs Li coverage. (a) clean (b) 1.0 ML Li](image)
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 $k_{||}$. While we lack detailed theory, we are nonetheless motivated to develop a simple picture of the spin ordering.

Fig. 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 $90^\circ$ sector and symmetrized to get the $180^\circ$ 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 apparent in the image, these are all assigned to unrelated bulk and surface states, and in any case are also present for W.

Why should these states and their Fermi contours be so interesting? They should 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) [6-8]. 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 [18]. 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. Finally, these spin orderings will very likely impact the interfacial magnetic structure between a heavy metal like tungsten and a magnetic metal, a topic of intense current interest.

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 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. This work was supported by the Department of Energy under grant DE-FG06-86ER45275. JWC was supported by the Seo-Am Fund.
