LBNL-42027
LSBL-476
Preprint

ERNEST ORLANDO LAWRENCE
BERKELEY NATIONAL LABORATORY

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

Eli Rotenberg, J.W. Chung, and S.D. Kevan

Advanced Light Source Division

July 1998

Submitted to
Physical Review Letters

REFERENCE COPY
Does Not
Circulate
Bldg. 50 Library - Ref.
Lawrence Berkeley National Laboratory

LBNL-42027
Copy 1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBNL-42027
LSBL-476

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

Eli Rotenberg

Advanced Light Source Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, California 94720

J.W. Chung

Department of Physics
Pohang Institute of Science and Technology
Pohang, Korea

and

S.D. Kevan

Department of Physics
University of Oregon
Eugene, Oregon 97403

July 1998

This work was supported by the U.S. Department of Energy at the University of Oregon (DE-FG06-86ER45275), and the Seo-Um Fund through the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory.

Spin-orbit-coupling induced surface band splitting in Li/W(110) and Li/Mo(110)

Eli Rotenberg
Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley CA 94720

J. W. Chung
Department of Physics, Pohang Institute of Science and Technology, Pohang, Korea

S. D. Kevan
Department of Physics, University of Oregon, Eugene OR 97403

(July 1, 1998)

Light Source Note:
Author(s) Initials EF 7/1/98 Date
Group Leader's initials 7/2/98 Date

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.

PACS numbers:73.20.At, 63.20.Kr, 73.20.Mf

Under what circumstances can a material that is non-magnetic 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 isoelectronic 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 ~ 0.5 eV for W(110), but only ~ 0.1 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.

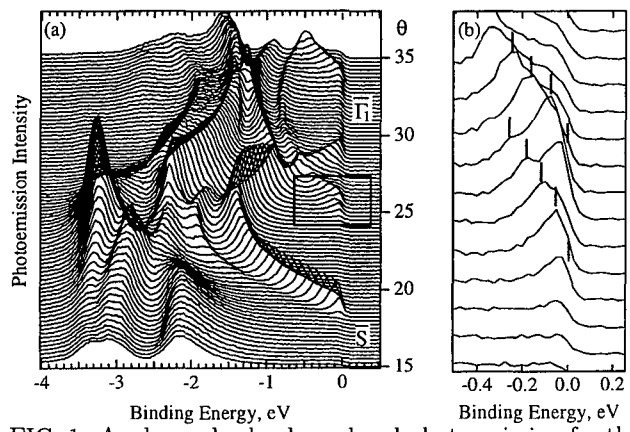

FIG. 1. Angle-resolved valence band photoemission for the clean W(110) surface. (a) Series of individual spectra vs polar angle θ. (b) Same as the rectangular region in (a).

We prepared the clean crystals using standard techniques [10]. Lithium was deposited from well-outgassed SAES getters held ~ 1 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 1*s* 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 $\sim$ 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 $k_{\|} = 0.5124(h\nu + E - \Phi_W)^{1/2} \sin\theta$, where E is negative, Φ_W is the work function, and $h\nu = 100$ 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 $h\nu = 100.0$ eV as a function of polar angle for the clean W(110) surface. Fig. 1(a) shows spectra taken with $15° < \theta < 35°$, a range which roughly spans from the boundary of the first SBZ (denoted $\overline{S}$) to the center of the second SBZ (denoted $\overline{\Gamma}_1$). 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 $\theta \sim 26°$, 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 $k_{\|}$. 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 Papaconstantopolous [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

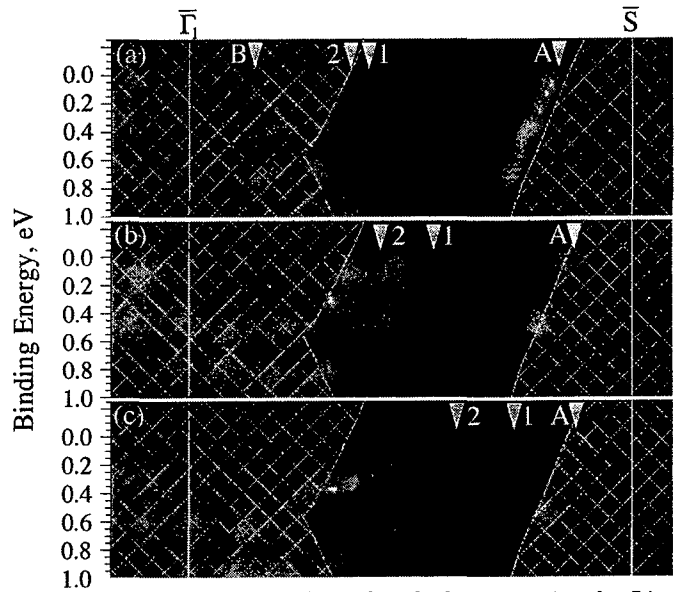

FIG. 2. Angle-resolved valence band photoemission for Li on W(110) vs Li coverage. (a) clean W(110) (b) $\sim$ 0.5 ML Li (c) 1.0 ML Li. The bands in (b,c) appear discontinuous since fewer angles were sampled than for (a).

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 $\sim$ 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 $\overline{\Gamma}$, a possible manifestation of the surface state $\rightarrow$ 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

mapping results for the clean Mo(110) surface. Here we scanned from zone center at normal emission (denoted $\overline{\Gamma_0}$) to $\overline{S}$rather than in the second SBZ because for Mo the intensity of the surface states was strongest there. We see a clear one-to-one correspondence between each band in Fig. 3(a) and Fig. 2(a), with the bands of the former located typically at 0.5 eV lower binding energy than the latter. The only difference, apparently minor for the clean surface, is that whereas for W we see barely two states 1 and 2, in 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 upon Li adsorption. Fig. 3(b) shows that a similar splitting develops in band 1+2 upon Li exposure which, while small, is apparent in several spectra on either side of $\overline{\Gamma}$at binding energy ~ 0.6 eV. The maximum observed splitting is much less for Mo(110) (about 0.13 eV) than for W(110) (about 0.5 eV). While there is a weaker, unrelated bulk feature near 1+2 for the clean surface which might affect our interpretation, our conclusions remain unchanged when we examined equivalent surface bands in another SBZ where the bulk transition is absent.

In line with previous work by Jensen, et al. [1], on Au(111), we propose the splitting between bands 1 and 2 to be due to the spin-orbit interaction, given by the Hamiltonian

$$H_{\mathrm{SO}} = (\hbar^2/4m^2c^2)(\vec{\nabla}V \times \vec{p}) \cdot \vec{\sigma}. \qquad (1)$$

The high nuclear mass of tungsten compared to molybdenum makes relativistic effects much more important for tungsten. The magnitude of the band splitting, while 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 [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 continuum) 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.

Why should the splitting evolve with Li coverage? Note first that the splitting would vanish in the presence of inversion symmetry; bands in centrosymmetric systems are Kramers degenerate [17]. Given that both tungsten and molybdenum are centrosymmetric in the bulk, the surface itself is required for the proposed splitting to occur. According to Eq. 1, the magnitude of the

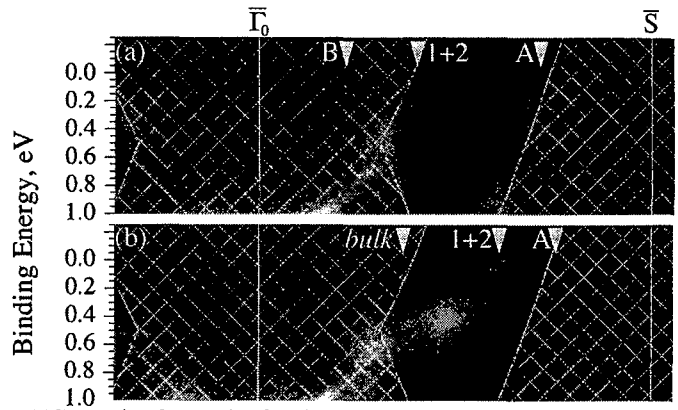

FIG. 3. Angle-resolved valence band photoemission for Li on Mo(110) vs Li coverage. (a) clean (b) 1.0 ML Li

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 phonon anomalies also indicates qualitatively that they are not highly surface localized [5,6].

By contrast state 1+2 must be relatively surface-localized and can therefore sample the surface potential gradient more effectively. Moreover, as more alkalis are adsorbed, the state shifts further into the gap and become even more localized, leading to a larger splitting. The fact that the energy splitting is not a monotonic function of depth in the gap, however, implies that 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 $\vec{\nabla}V$ 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 $k_{\|}$. 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 $k_{\|}$. 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° 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 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.

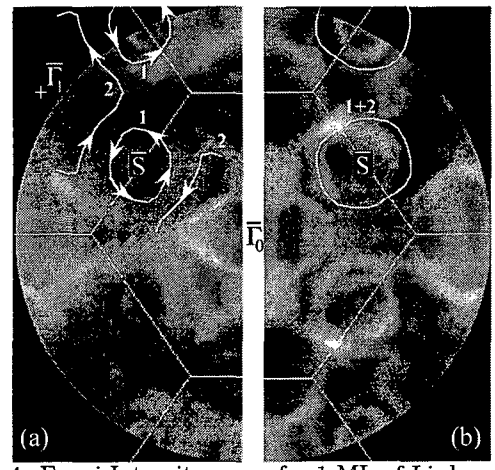

FIG. 4. Fermi Intensity maps for 1 ML of Li deposited on (a) W(110) and (b) Mo(110). The straight white lines are the surface Brillouin Zone boundaries; the remaining white lines in the upper part denote the Fermi crossings, derived from the mirror-reflected raw data (lower part).

[1] S. LaShell, B. A. McDougall, and E. Jensen, Phys. Rev. Lett. **77**, 3419 (1996).
[2] S. D. Kevan and R. H. Gaylord, Phys. Rev. B **36**, 5809 (1987).
[3] R. Paniago, Surf. Sci. **336**, 113 (1995).
[4] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1983).
[5] E. Hulpke and J. Ludecke, Phys. Rev. Lett. **68**, 2846 (1992).
[6] M. Balden *et al.*, Surf. Sci **307-9**, 1141 (1994).
[7] C. Bungaro, S. d. Gironcoli, and S. Baroni, Phys. Rev. Lett. **77**, 2491 (1995).
[8] B. Kohler *et al.*, Phys. Rev. Lett. **74**, 1387 (1995).
[9] B. Kohler *et al.*, Z. f. Physikalische Chemie **197**, 193 (1995).
[10] R. H. Gaylord, K. Jeong, and S. D. Kevan, Phys. Rev. Lett. **62**, 203 (1989).
[11] R. D. Diehl and R. McGrath, Surf. Sci. Rep. **23**, 43 (1996).
[12] T. Warwick, Rev. Sci. Inst. **66**, 2037 (1995).
[13] S. D. Kevan and W. Eberhardt, in *Angle-Resolved Photoemission*, edited by S. D. Kevan (Elsevier, Amsterdam, 1992).
[14] D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).
[15] E. Kneedler *et al.*, Phys. Rev. Lett. **64**, 3151 (1990).
[16] E. Rotenberg and S. D. Kevan (unpublished).
[17] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University, Cambridge, 1972).
[18] E. Rotenberg and S. D. Kevan, Phys. Rev. Lett. **80**, 2905 (1998).

Ernest Orlando Lawrence Berkeley National Laboratory
One Cyclotron Road | Berkeley, California 94720

Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098