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Spin-orbit-interaction-induced surface resonance on W(011)

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A surface resonance has been observed on the (011) surface of tungsten using angle-resolved photoemission. The resonance is located near the center of the surface Brillouin zone in a pseudogap opened by the spin-orbit interaction. It is degenerate with a bulk band, which in the absence of the spin-orbit interaction would have a different symmetry than a state in the gap. The resultant weak coupling leads to the formation of a well-defined resonance. These conclusions are supported by polarization- and photon-energy-dependent studies. The generality of our observations is discussed.

The precise characterization of clean surface electronic structure continues to be an active and fruitful area of research due to the variety of fundamental and technological questions it influences.[1-3] The stationary electronic states near a perfectly crystalline clean surface can be classified into three categories: bulk states which extend deep into the material and simply terminate at the surface, surface states which exist in projected bulk band gaps and are thus spatially localized near the surface, and surface resonances which have enhanced amplitude at the surface but which couple to bulk states of the same energy, parallel momentum, and symmetry. The degeneracy in energy makes surface resonances the most difficult to distinguish experimentally and to characterize theoretically from first principles. The classic ambiguity in this respect arose in the interpretation of the so-called "Swanson hump" on W(001), the first surface state observed on a metal surface.[4] Despite several years of theoretical and experimental input, it has only recently been determined that the feature is indeed a state, not a resonance, located in a symmetry-projected band gap.[5,6] To date, there exists no general procedure to predict when a surface resonance might occur and what its properties might be. This is unfortunate since resonant states enable communication between surface and bulk layers, and thus might be important in determining such phenomena as surface reconstruction and electric dipole formation.

The difficulty in predicting the occurrence of a surface resonance arises from the uncertainty of how strongly it will couple to the bulk states with which it is degenerate. Like a Fano or autoionizing resonance in atomic or molecular spectroscopy, a surface resonance will be lifetime broadened due to tunneling into the bulk continuum.[7] If the coupling is too strong, the resonance will be broadened to such an extent that it becomes too diffuse to observe. One needs to find circumstances under which the coupling is weak. One approach discovered several years ago[8] is to observe surface resonances on stepped surfaces which are coupled to bulk states by relatively weak umklapp scattering off the step superlattice. Another technique which has been suggested in various places,[9,10] but not accurately characterized before now, utilizes the broken symmetry implied by the spin-orbit interaction. In this case, the coupling to the bulk continuum is allowed only by spin-orbit scattering and will usually be weak. Using angle-resolved photoemission (ARP) to study W(011), we have characterized a surface electronic level near the center of the surface Billouin zone located in the "pseudogap" opened by the spin-orbit integration. As explained below, this level is weakly coupled to a bulk band at the same energy and is thus a resonance. This establishes a specific procedure for predicting the existence of a certain class of surface resonances.

Experiments were performed at the National Synchrotron Light Source at Brookhaven National Laboratory, using a photoemission spectrometer and soft-x-ray beamline described elsewhere.[11,12] A tungsten crystal was prepared by standard techniques,[13] and surface cleanliness and order were ensured using Auger electron spectroscopy and low-energy electron diffraction. The primary contaminant in the vacuum system at a base pressure of $(0.8-1.5)\times10^{-10}$ Torr was hydrogen. Photoemission spectra of this very hydrogen-sensitive resonance were stable for a period of 15 min, at which time the residual hydrogen could easily be removed by heating. The experimental energy and angular resolution were typically <100 meV and 1° full width at half maximum, respectively. Under these circumstances, a photoemission spectrum could be accumulated in 2–5 min.

Photoemission energy distribution curves collected for emission close to the W(011) surface normal under a variety of conditions are presented in Fig. 1. Curves (a) and (b) were collected at 20 eV photon energy with the photon polarization vector at 45° in the (100) mirror plane, for the clean surface and for a surface exposed to 0.4 L (1 L=1 langmuir$=10^{-6}$ Torr sec) of hydrogen. This corresponds to coverage of <0.2 monolayers. The clean surface spectrum is dominated by two broad features labeled B_1 and B_2, and by a narrow feature labeled SR (surface resonance) at a binding energy of 1.18 ± 0.04 eV. The extreme sensitivity to contamination of SR observed in (b) suggests significant amplitude at the surface. Curve (c) shows the normal emission spectrum accumulated at $h\nu=38$ eV. The feature labeled SR has not changed its binding energy position, but has decreased dramatically in intensity relative to the bulk features. The lack of dispersion and the variation in intensity with final-state momentum normal to the surface

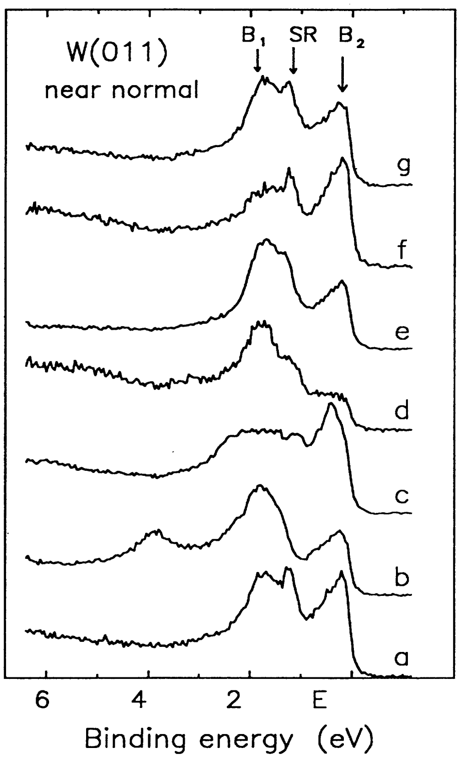

FIG. 1. ARP energy distribution curves of the tungsten (011) surface. (a) Clean surface at normal emission, 20 eV photon energy, 45° incidence, and polarization vector in the (011) plane. (b) As (a), but following exposure to 0.4 L of hydrogen. (c) As (a), but at photon energy of 38 eV. (d) As (a), but with the polarization vector in the (100) mirror plane. (e) As (a), but collected at an angle 3° from the normal in the (011) mirror plane. (f) and (g) As (a), but collected with the photons incident at 25° and 75° form the normal.

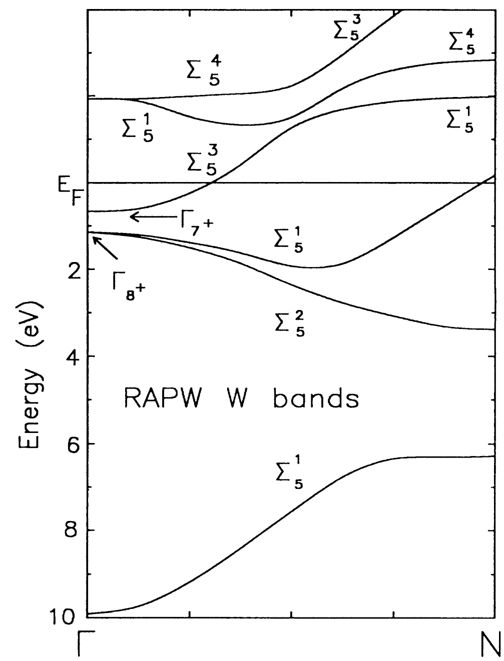

FIG. 2. Calculated band structures of tungsten along the [011] axis. Symmetry labels are subscripted with the double group representations and superscripted with the single group representations to which the bands would belong in the absence of spin-orbit coupling. Above the Fermi level, hybridization results in the changing of the single group labels roughly half-way from Γ to N.

$k_\perp$ are both in accord with what is expected for a surface electronic state.[1-3,14] Curve (d) was collected from the clean surface at $h\nu=20$ eV, but with the polarization vector at 45° in the (110) mirror plane. The surface feature is less intense relative to the bulk features when excited in this polarization than that used in (a). The next curve is taken with the same polarization as (a), but at an angle of emission of 3° from the normal. The surface feature was found to vanish rapidly for emission in both symmetry azimuths away from the normal. This presumably explains why it had not previously been characterized in detail.[15,16] The final two curves demonstrate the behavior of the surface feature upon changing the angle of photon incidence, and will be discussed further below.

The calculated relativistic band structure for tungsten along the [011] direction is shown in Fig. 2.[17] The symmetry labels of the bands have been subscripted according to the double group representation (Σ_5 in all cases[18]), and superscripted according to what would be the appropriate representation if the spin-orbit interaction were neglected. In the doubled representations, the only projected gap below the Fermi energy along this line, which forms the $\bar{\Gamma}$ point of the surface Brillouin zone, occurs between bands one and two. This lies too low in energy to be related to the features observed in Fig. 1. Both features, in fact, lie close to the bottom of the calculated "pseudogap" between Γ_{8+} and Γ_{7+} opened by the spin-orbit interaction. We refer to this as a pseudogap because the only degenerate bulk band is of Σ_5^1 symmetry. An electronic energy level in the pseudogap having substantially different residual single-group character will be coupled only weakly by the spin-orbit interaction to the Σ_5^1 continuum, and thus a well-defined surface resonance might be able to exist. We interpret the feature labeled SR in Fig. 1 in this fashion, and support this interpretation in the following paragraphs.

Part of this support comes from the photon energy dependence of the SR emission. In the simplest direct-transition model, bulk states near the Γ point of the bulk zone are sampled for $h\nu=20$–24 eV.[1-3] One would expect to see the two bulk bands at the top and bottom of the pseudogap at this photon energy. The occurrence of a third, sharper peak between two broader ones suggests a surface-localized state within the pseudogap. Moreover, surface state intensities are known to maximize in intensity when the final momentum probes the bulk band edges.[14] One would expect similar observations for a surface resonance, in general accord with our observations in Figs. 1(a) and 1(c). A more complete photon-energy-dependent analysis of the W(011) data[19] places the surface feature 0.27 ± 0.02 and 0.47 ± 0.02 eV from the lower and upper band edges, respectively. It should be pointed out that to assign the observed energies of features B_1 and B_2 to the band energies Γ_{8+} and Γ_{7+} would be seriously in error, since these spectral features are broadened significantly by density-of-states emission, and it is well known that the presence of a surface feature disturbs the emission profile of nearby bulk bands.[14]

Additional support for our interpretation comes from the polarization dependence of the emission intensity. The presence of the spin-orbit splitting in C_{2v} symmetry makes the polarization dependences nonrigorous since all eigenstates are of Σ_5 symmetry in the double group and thus are observable in principle for all polarizations. There will, however, be residual polarization dependences governed by the single group symmetries which allow us to determine the superscripts in Fig. 2 provided the perturbations due to the spin-orbit interaction are not too large compared to the bandwidth of the unperturbed system. With the polarization vector in the (100) [(011)] mirror plane, we excite Σ_5^1 and Σ_5^3 [Σ_5^1 and Σ_5^4] states preferentially.[20] Since the surface resonance is more intense when the polarization is in the (100) mirror plane, we determine that the SR feature should be labeled either Σ_5^1 or Σ_5^3 symmetry. These two labels can in principle be distinguished by the photon incidence measurements shown in Figs. 1(f) and 1(g). The former of these was collected at 25° incidence and will emphasize Σ_5^3 states, while the latter was collected 75° incidence and will emphasize the Σ_5^1 states. The relative intensities of features B_1 and B_2 are observed to follow this prediction, but the surface feature is apparently of mixed symmetry since its relative intensity is not strongly polarization dependent. The resonance is intimately related to the spin-orbit interaction, and should not be expected to follow the single group propensity rules. In addition, the coupling to bulk states which do exhibit remnant single-group symmetry will be weak, and a well-defined resonance can exist.

It is important to speculate upon the generality of the occurrence of spin-orbit-induced surface features. Previous interpretations[21] of the Swanson hump feature on W(001) were similar to our interpretations here, but the two most recent calculations demonstrate that it is a true state in a hybridization gap. It is thus not intimately related to a spin-orbit gap. There exist in the literature two observations of intrinsic surface states located in spin-orbit band gaps.[22,23] The present state exists within gaps opened by the spin-orbit interactions, but it is a resonance because the spin-orbit coupling lowers the symmetry of all bands to Σ_5. A lowering of the magnitude of the spin-orbit coupling will reduce the size of the pseudogap, tending to make a split-off state less likely, but this is accompanied by weaker coupling to bulk states which would make a resonance more well defined. We have observed a similar state molybdenum.[24] Chromium will be more complicated due to its magnetic structure. We speculate that this specific effect will be rather general.

A different way in which the spin-orbit interaction can produce a surface resonance is to eliminate a mirror plane of symmetry, thereby weakly coupling a state in a symmetry-projected gap to a continuum of the other symmetry. This has been suggested elsewhere,[6] and indeed has been observed without comment in many surface "states" where the possibility of spin-orbit broken symmetry was not considered. While we have observed this effect in several states on W(011) and Mo(011),[19,24] this is a distinct effect from what we report here, where the state is intrinsically produced by the spin-orbit interaction.

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