Spin Splitting of an Au(111) Surface State Band Observed with Angle Resolved Photoelectron Spectroscopy

S. LaShell, B. A. McDougall, and E. Jensen
Physics Department, Brandeis University, Waltham, Massachusetts 02254
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High momentum resolution angle resolved photoemission spectra from the Au(111) sp-derived surface state exhibit a doublet. The separation between the peaks increases linearly with $k_{\|}$, and reaches a maximum of 110 meV at 0.153 Å^{-1}, when one of the bands crosses the Fermi level. These results are interpreted as spin-split surface state bands, with the spins aligned in the plane of the surface perpendicular to the electronic momentum. The origin of the splitting is spin-orbit coupling, which can break spin degeneracy in systems which lack inversion symmetry. [S0031-9007(96)01452-4]

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Spin-orbit coupling (SOC) is well known to split degeneracies between one electron energy levels in atoms, molecules, and solids [1]. It has its origin as one of the relativistic corrections to the Schrödinger equation, and takes the form $H_{\mathrm{SOC}} = (\hbar/4mc^2)(\nabla V \times \vec{p}) \cdot \vec{\sigma}$, where V is the external potential, $\vec{p}$ is the momentum, and $\vec{\sigma}$ is the Pauli spin operator. With some further approximation, the interaction can be written as proportional to $\vec{L} \cdot \vec{S}$, where $\vec{L}$ and $\vec{S}$ are the orbital and spin angular momenta. This form suggests that a twofold degenerate (spin only) level might be spin split by SOC into levels with spin parallel and antiparallel to the orbit. However, such splitting is symmetry forbidden for systems with a center of inversion, and most solids do not have spin degeneracy broken by SOC [1]. The absence of an inversion center at the crystal surface breaks this symmetry, and permits surface state levels with the same parallel wave vector $\vec{k}_{\|}$ and opposite spins to have different energies.

The structure of the resulting slit bands can be seen in a nearly free electron (NFE) model, the simplest model that contains a surface state. The magnitude of the NFE splitting is unphysically small, as NFE explicitly ignores the region near the ion cores where the effect of SOC is largest. The qualitative behavior, however, appears to be correct for sp-derived surface states near the center of the surface Brillouin zone (SBZ) $\overline{\Gamma}$. Let the crystal exist in the half plane $x < 0$, with potential $V(\vec{r}) = \theta(-x)(U_0 + U_1 e^{iKx} + U_1^* e^{-iKx})$, where K is the magnitude of a reciprocal lattice vector $\vec{K}$ in the normal ($\hat{x}$) direction. Under reasonable conditions and in the absence of SOC, a (spin degenerate) surface state with $\vec{k}_{\|}$ (magnitude k, and in the $\hat{y}$ direction for definiteness) exists and has the form $\Psi(r) = e^{iky} e^{\lambda x} \cos(Kx/2 + \phi)$ for $x < 0$ and $\Psi(r) = e^{iky} e^{-\beta x} \cos(\phi)$ for $x > 0$. ϕ, λ, and β are constants determined by K, U_0, and U_1 [2]. If the surface state and its spin partner are well separated in energy from all other levels with the same parallel momentum, then first order perturbation theory allows one to find the resultant splitting and spin structure by diagonalizing H_{SOC} in the two dimensional subspace of surface states of fixed $\vec{k}_{\|}$. Note that, with this choice of coordinate system and with $\vec{k}_{\|}$ along $\hat{y}$, $\nabla V \times \vec{p}$ is in the $\hat{z}$ direction. Since σ_z is diagonal, so is H_{SOC}. The spins are split along $\hat{z}$, and the energy splitting can be found by evaluating the diagonal matrix elements. Similar analyses for other directions of $\vec{k}_{\|}$ show that the spin axis remains in the plane of the surface, but rotates around, remaining perpendicular to $\vec{k}_{\|}$ as shown in Fig. 1. The NFE matrix elements yield splittings proportional to k, and of order 10^{-6} eV.

As mentioned above, the small size of the splitting is an artifact of NFE. This wave function is better thought of as a pseudo wave function, and the effects of the core region can by treated by modifying H_{SOC} [3,4]. The

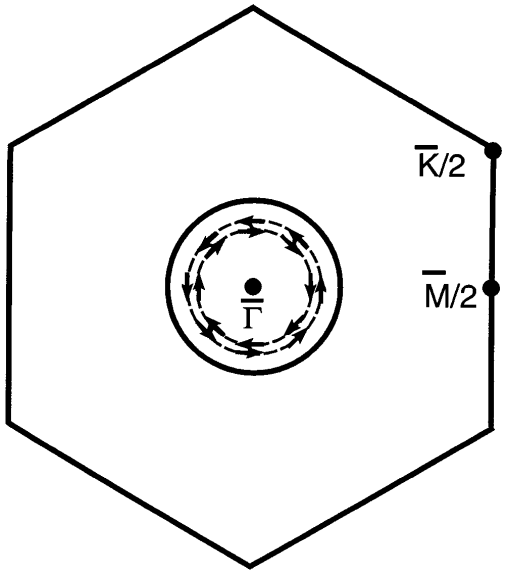

FIG. 1. A view of the Fermi surfaces and (one half of) the surface Brillouin zone for Au(111). The arrows and dashed lines indicate the spin orientations for the proposed surface Fermi surface, and the solid line represents the bulk Fermi surface neck. All spins are in the plane of the surface. For the surface, $k_f = 0.153, 0.177$ Å^{-1}, and $\overline{M} = 1.26$ Å^{-1}, while $k_f = 0.216$ Å^{-1} in the bulk.

modified Hamiltonian takes the form $H'_{\mathrm{SOC}} = (\epsilon/\hbar)\vec{L} \cdot \vec{\sigma}$ for distances from the nucleus smaller than a model radius R_M, and zero elsewhere [4]. ϵ is an energy of order the relevant atomic spin-orbit splitting. $\langle L_x \rangle = \langle L_y \rangle = 0$ by symmetry, and $L_z = -i\hbar x(\partial/\partial y) = \hbar k x$, where x is measured with respect to the ion position. Since $\vec{L}$ is along $\hat{z}$ and proportional to k, the structure is the same as in NFE; the spins are polarized in the plane, perpendicular to the electron momentum. $\Delta E = 2\epsilon k\langle x \rangle$ [5]. The atomic splitting of the $6p$ level in Au is 0.47 eV [6], while $\langle x \rangle$ should be of order $R_M \sim 1$ Å [4]. Thus, at the Fermi momentum of 0.15 Å^{-1}, $2\epsilon k\langle x \rangle \sim 0.15$ eV, and splittings of order 0.1 eV are reasonable for this Au(111) surface state. The precise value, and even the sign of the splitting, will depend on details of the shape of the (pseudo) wave function near the ion.

The Au(111) $\overline{\Gamma}$ surface state has been extensively studied. Three relatively recent angle resolved photoemission (ARP) investigations are [7–9]. This state is very similar to the other noble metal (111) $\overline{\Gamma}$ surface states, and exists in the bulk Fermi surface neck near L. Previous room temperature studies report normal emission binding energies of 0.41 eV [7,9] and 0.44 eV [8], a Fermi momentum of 0.173 Å^{-1}, and normal emission widths of 158 [7], 280 [8], and 135 meV [9]. The Au surface suffers from a complex reconstruction, extensively studied by electron [10], helium atom [11], and x ray diffraction [12], and by scanning tunneling microscopy [13].

The spectrometer is described in [14]. All data shown are taken with ArI resonance radiation, which is a doublet, $\hbar\omega = 11.62, 11.83$ eV. The electron analyzer is a 50 mm hemispherical analyzer with 0.5×5 mm^2 entrance and exit slits, and 4×20 mR angle determining apertures. Typical instrumental energy resolution for the spectra shown is 25 meV. Typical count rates are near 10 Hz in the peak. The surface was prepared by extensive sputter anneal cycles. This ARP study of the Au(111) $\overline{\Gamma}$ surface state differs from previous studies mainly by its high angular resolution.

Room temperature data along the $\overline{\Gamma}$-$\overline{M}$ line are presented in Fig. 2. The 210 eV higher binding energy satellite is from the Ar doublet. The peaks are fitted to Lorentzian line shapes with linear background and Fermi function and the fitted curves are shown. It is clear from these data that there is one (resolvable) peak for small values of k, which smoothly splits into two for larger k. The widths are near 90 meV for $\overline{\Gamma}$, increasing to about 100 meV for larger k. This increase in width with k is mostly, and perhaps entirely, an effect of the instrumental momentum resolution. All widths are about twice as large as seen for the corresponding state on Cu(111) [14], and are difficult to understand quantitatively. They are, however, much narrower than seen in previous studies of the Au(111) surface [7–9]. We believe that the larger widths seen in other investigations are the result of poorer angular resolution and lower surface quality. The doublets

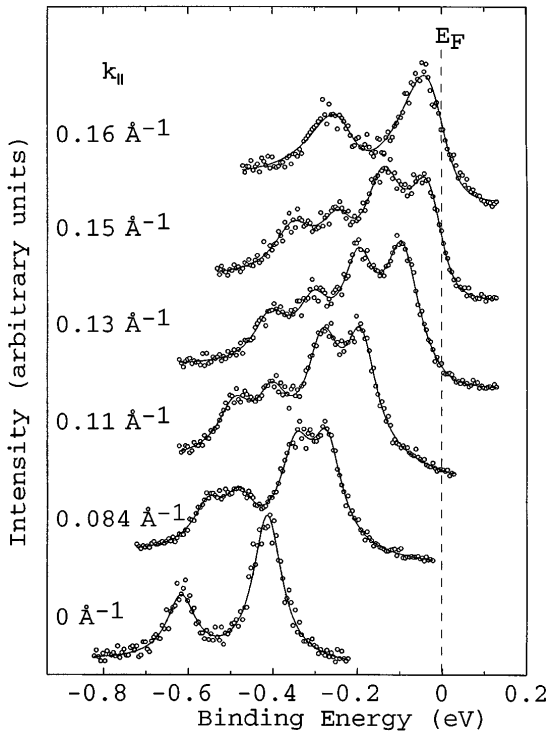

FIG. 2. Spectra taken along the $\overline{\Gamma}$-$\overline{M}$ at indicated values of parallel momenta. The 210 meV higher binding energy satellite is from the Ar satellite. Data are open circles, while the solid line is a fit to (four) Lorentzian peaks with linear background and Fermi function. The observed splitting is interpreted as the energy difference between the two spin orientations indicated in Fig. 1. The number of counts in the peaks varies from 200–1000.

seen in this study easily fit "inside" the peak widths seen in previous studies, perhaps explaining why this splitting was not reported before.

Peak positions from fits like those in Fig. 2 are shown vs momentum in Fig. 3. These positions are fit to two parabolas, with results as shown. The fit results show two bands of similar intensity and width exhibiting nearly identical dispersion, but offset in k space by 0.023 Å^{-1}. The two Fermi momenta are 0.153 and 0.176 Å^{-1}. The maximum observed energy difference of 110 meV between the two bands occurs at the lower Fermi momentum. Dispersion and peak splitting measured in the $\overline{\Gamma}$-$\overline{K}$ direction are not significantly different. Dispersion measured with HeI radiation (21.2 eV) gives the same separation between the peaks as a function of momentum. Data taken at 140 K exhibit similar behavior (slightly higher initial binding energy, as seen by [8] and [9], and smaller peak widths, but nearly identical splitting).

These data are consistent with an interpretation as SOC spin-split surface state bands. There are three points of agreement. First, the magnitude: This picture predicts a splitting of order 0.15 eV for the Au(111) $\overline{\Gamma}$ surface state at k_f, in good agreement with the observation of 0.110 eV. Second, the dependence on k: The linear

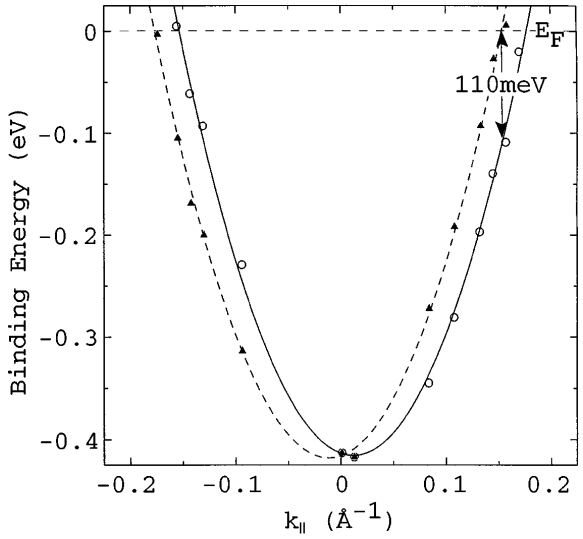

FIG. 3. E vs k dispersion from fits like those in Fig. 2. Data are open circles and filled triangles; the solid and dashed lines are parabolic fits. The fit results are (eV and Å^{-1}): $E_1(k) = 15.2(k - 0.0117)^2 - 0.416$, and $E_2(k) = 15.3(k + 0.0117)^2 - 0.418$.

terms in the dispersion $(\pm)\epsilon k\langle x\rangle$ can be added to the quadratic term characteristic of any NFE band to produce two parabolas with the same dispersion, but with their minima offset from $k = 0$. As shown in Fig. 3, the fit to two parabolas with the same dispersion and maximum binding energy is excellent. Finally, the intensities of the two peaks: The two peaks should, and do, have nearly identical intensities, as the real space wave functions are identical, and each corresponds to a singly occupied electron level.

It is important to rule out other possible explanations of the split peaks. It is unlikely that there are two conventional surface state bands on this surface. Cu(111) and Ag(111) are very similar surfaces to Au(111). Extensive theoretical and experimental studies of these materials do not exhibit split bands. The major difference between Au and these materials is the much larger SOC in Au (atomic $p_{3/2}$-$p_{1/2}$ splittings are 0.47, 0.11, and 0.03 eV for Au, Ag, and Cu, respectively [6]). Calculations of the electronic structure of Au(111) do not predict two peaks [15].

A twinned crystal could yield two peaks that would disperse as shown in Fig. 2. This explanation would require that data taken with larger photon energy exhibit the same splitting in angle, and a different splitting in momentum, while our data with HeI radiation exhibited the same momentum splitting. Additionally, it would likely require different behavior in the $\overline{\Gamma}$-$\overline{K}$ direction, which is not observed.

More problematic, one can imagine mechanisms whereby the reconstruction of the surface generates splitting of the surface state band. The reconstruction consists of a uniaxial compression of the surface layer along the $(1\overline{1}0)$ (or $\overline{\Gamma}$-$\overline{K}$) direction; the compression magnitude (4.5%) is such as to come back into registry every 22 atoms. This compression can also be thought of as the surface atom alternating between the face centered cubic (fcc) bulk-termination site and the hexagonal close packed (hcp) bulk-termination site. There are three symmetrically equivalent $(1\overline{1}0)$-like axes in the surface, and domains of order a few hundred Å along each direction are formed. There are also larger length scale structures described in [12,13].

We have considered three types of reconstruction-based explanations, and each fails to explain substantial parts of the data. The simplest explanation is that the extra peak occurs because of diffraction of the surface state or of the excited photoelectron by the potential associated with the reconstruction. There are two problems with this explanation. First, the separation of the peaks in momentum space (0.023 Å^{-1}) is nearly 5 times smaller than the dominant reconstruction reciprocal lattice vector (0.11 Å^{-1}). Second, the intensity ratio of the peaks (unity) indicates very strong diffraction, so that more than two peaks ought to be observed.

A second explanation considered is that emission somehow occurs independently from the fcc and hcp domains; each peak corresponds to emission from one region. This explanation appears attractive because the peaks have similar intensities, and the fcc and hcp regions occupy similar areas. There are two problems with this interpretation. First, each region would include only 10–15 atoms in the $(1\overline{1}0)$ direction, so that only 15 levels would be defined in the entire zone, of which only 1/10th (one or two levels) are occupied; this should lead to observable size effects. Second, when the bands from the two regions overlap as these do, the two states should hybridize and lose their regional identities. This explanation then becomes identical to the diffraction explanation, and inherits all of its difficulties.

The third explanation considered is that anisotropy of the compression causes anisotropy in the dispersion of the surface state. There are three different domains of reconstruction imaged at all times, making two different angles with respect to $\vec{k}_{\|}$; each peak might be characteristic of one orientation. The major flaw in this explanation is that the observed peaks have similar intensities, whereas this picture requires an intensity ratio of 1/2. Another problem is that the behavior ought to be different along $\overline{\Gamma}$-$\overline{K}$ than along $\overline{\Gamma}$-$\overline{M}$ because the angles will be substantially different. This is not observed.

Overall, we find the spin-splitting explanation much more satisfactory than any of the alternatives we have considered, and tentatively accept it. Explicit verification could come from a fully relativistic calculation of the surface electronic structure, or from a spin polarized ARP experiment. Similar effects should occur with all sp-derived surface states near $\overline{\Gamma}$. States in other gaps, and d-like states should also be split, but the structure may be different. The size of this effect will be very small

in light materials, but might be comparable to the 0.1 eV observed here for other $5d$ materials.

These are interesting electrons. $|\vec{k}_{\|}\uparrow\rangle$ and $|-\vec{k}_{\|}\downarrow\rangle$ are degenerate, as demanded by time reversal symmetry. While an excess of one spin is expected in the positive $\vec{k}_{\|}$ direction (a larger fraction of the SBZ is occupied by this spin orientation than by its partner), it is canceled by an excess of the opposite spin in the negative $\vec{k}_{\|}$ direction for no net spin density. Unfortunately, these states only comprise about 3% of an electron per surface atom, and will be difficult to detect with techniques that are not particularly selective. They should lead to strongly spin polarized ARP emission independent of the polarization of the light, although given the required angular resolution the count rate will be very low. There should be some evidence of an 0.1 eV loss peak in electron energy loss spectroscopy for the transition from one band to its spin partner for zero momentum transfer. Since these states cross the Fermi level, they should participate in thermal and dc field effects. They will not, however, behave as normal metal electrons near the Fermi level. They are not free to orient along an external magnetic field, and should be essentially inert to magnetic fields perpendicular to the surface. There is a small one electron energy, or order 20 μeV per surface atom, derived from occupying the lower energy level for a larger fraction of the SBZ than the higher energy level. There should be a small force associated with this energy that will act to move the atoms towards regions where $\langle x\rangle$ for the surface state wave function is largest. Similar behavior of interface states may be important for understanding the electronic structure of high-Z layered materials.

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