PHYSICAL REVIEW B VOLUME 33, NUMBER 6 15 MARCH 1986

Relativistic effects on the surface electronic structure of Cu(001): Observation of a spin-orbit-gap surface state

P. L. Wincott, N. B. Brookes, and D. S.-L. Law*
Chemistry Department, Manchester University, Manchester M13 9PL, United Kingdom

G. Thornton†
Chemistry Department, Manchester University, Manchester M13 9PL, United Kingdom and Science and Engineering Research Council, Daresbury Laboratory, Warrington WA4 4AD, United Kindgom

(Received 1 November 1985)

A second Cu(001) $\bar{M}$ surface state located near the d-band maximum has been characterized using angle-resolved photoemission. High-energy resolution, provided by a new dispersive spectrometer, was necessary to identify and characterize the surface state. At $\bar{M}$ the state, which has odd parity with respect to the (100) mirror plane, lies 65 meV below the d-band maximum, at 2.113-eV binding energy. Comparison with the surface projection of a recently calculated relativistic bulk band structure, indicates that this states lies in an absolute spin-orbit gap. The gap extends along one-third of $\bar{\Sigma}$ in the surface Brillouin zone.

The low-Miller-index planes of copper have been extensively employed as model systems in the study of transition-metal surface electronic structure by angle-resolved photoemission (ARP).[1-10] Corresponding surface electronic structure calculations have been performed;[11-14] the most recent[13] to high numerical accuracy, with considerable agreement in their results. They predict numerous occupied surface states and resonances throughout the surface Brillouin zones (SBZ), several of which have been identified experimentally.[4-9] Recently, however, Cu(110) surface states (resonances) have been identified[2] which were not predicted by a corresponding self-consistent slab calculation. Cord, Courths, and Wern[2] suggested that they might arise from relativistic (spin-orbit coupling) effects, which are known to modify the bulk band structure.[10,15]

In the case of Cu(001), the predicted Tamm states near the top of the d bands are of special interest.[12,13] These states are pushed out of the bulk continua by an increased Coulomb repulsion term arising from excess s,p electron density at the surface.[13] The slab calculations suggest that they give rise to a large density of surface states,[12] which might be expected to interact strongly with chemisorbed species. Indeed, angle-integrated photoemission spectra of Cu(001) show an attenuation in the region of the d-band maximum following adsorption of N_2, O_2, etc.[3] Throughout most of the SBZ the calculated energy positions of Tamm states lie very close to, or within, the d-band continua, and are therefore difficult to identify experimentally. However, at $\bar{M}$, one such state is predicted to lie 550 meV (Ref. 12) to 660 meV (Ref. 13) above the upper d-band continuum. This $\bar{M}_2$ state consists of d_{xy} orbitals with the axes shown in Fig. 1 ($d_{x^2-y^2}$ orbitals using slab-adapted axes, where z is the surface normal and x,y are nearest-neighbor directions[13,14]), which have little interaction between planes perpendicular to the surface normal. Previous ARP studies have located this state at 1.8-eV binding energy, 200 meV above the d-band maximum at $\bar{M}$.[4-9] The existence of a further two $\bar{M}$ Tamm states near the d-band maximum has been predicted.[11-14]

In this Rapid Communication we describe angle-resolved photoemission results which identify and characterize a surface state lying 65 meV *below* the d-band maximum at $\bar{M}$. This state is not one of the predicted Tamm states, but rather a Shockley state lying in a spin-orbit gap. Its existence demonstrates, in a rather dramatic manner, that relativistic effects can play an important role in determining the surface electronic structure of first-row transition elements.

The ARP experiments were performed using an instrument constructed by Vacuum Science Workshop Ltd. which will be described in detail elsewhere.[16] Briefly, it consists of a 180° hemispherical analyzer of 45-mm mean radius with three-element input and exit lenses. The position of the analyzer is continuously adjustable in two planes of rotation. In the experiments described here unpolarized HeI ($h\nu = 21.2$ eV) radiation was incident in the ΓXWK plane at 55° to the Cu(001) surface normal. Spectra were recorded at various electron emission angles (θ_e) in the ΓXWK

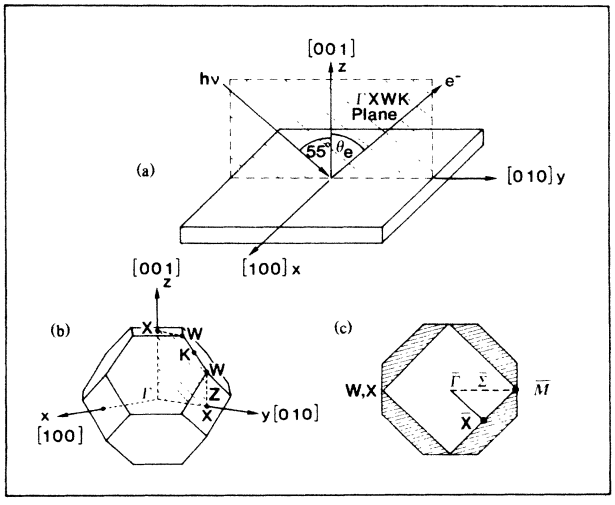

FIG. 1. (a) Experimental geometry. (b) The fcc Brillouin zone with the ΓXWK plane shaded. (c) The Cu(001) surface Brillouin zone superimposed on the bulk zone projection.

azimuth. The experimental geometry is shown in Fig. 1. The angular resolution employed in this work was $\pm 1.8°$ and the energy resolution was $\Delta E = 16$ meV [full width at half maximum (FWHM)].

The Cu(001) crystal was cleaned in the experimental chamber (base pressure $< 8 \times 10^{-11}$ mbar) by repeated cycles of argon-ion bombardment and annealing. Following this treatment, Auger spectroscopy revealed a carbon contamination level of $< 3\%$ monolayer and the sample gave a sharp (1×1) low-energy electron diffraction (LEED) pattern. Orientation of the sample azimuth was accomplished initially using LEED, and subsequently by maximizing the intensity of the 1.8-eV binding energy $\bar{M}_2$ surface state.

Selected ARP spectra recorded at polar emission angles in the range $(35° < \theta_e < 65°)$ with respect to the surface normal of Cu(001) are shown in Fig. 2. The sample temperature during these measurements was 150 K. Peaks B_1 and B_2 have previously been identified as bulk direct transition features. At $\bar{M}$, B_1 arises from a flat bulk d band derived from near the X_5 point,[5,8] and S_1 is the $\bar{M}_2$ Tamm surface state.[1,4-9] The features labeled S_2 were not resolved in the earlier work.[5,8] While there has been agreement on the energy position of S_1, there is debate about its natural linewidth at $\bar{M}$. Kevan, Stoffel, and Smith[7] reported a value of 40 meV, whereas Heimann, Hermanson, Miosga, and Neddermeyer[4] estimated the natural linewidth to be 6 meV, using a straight line extrapolation of analyzer pass energy versus peak width. In this work, the FWHM for S_1 at $\bar{M}(\theta_e = 61.5°)$ is 28 meV, the smallest band width reported to date. Taking the resolution of the analyzer, 16 meV, into account, the natural linewidth (inverse lifetime) of S_1 is 23 meV. Further discussion of phonon and lifetime broadening of this state will be described elsewhere.[16]

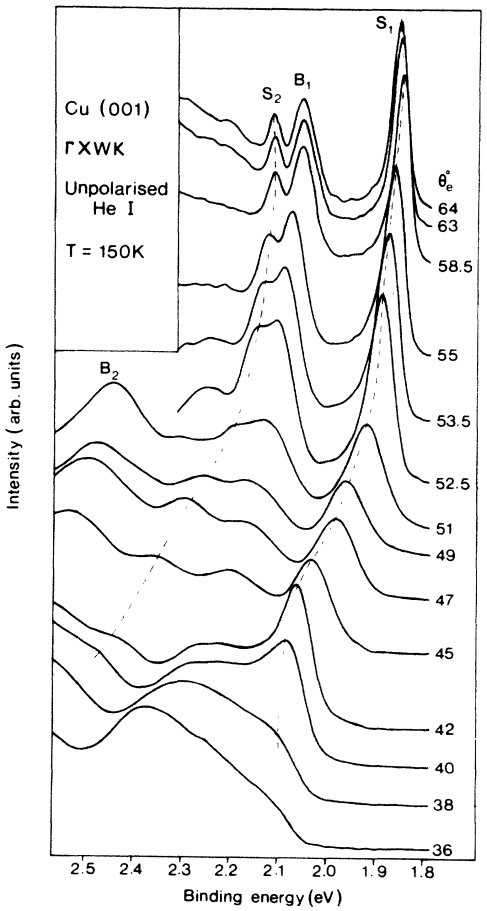

FIG. 2. Angle-resolved photoemission spectra ($h\nu = 21.2$ eV) of Cu(001) recorded with the experimental geometry shown in Fig. 1(a). The features labeled S_1, S_2, B_1, and B_2 are described in the text.

In this Rapid Communication, attention is focused on S_2, the surface character of which can be demonstrated by comparing He I and He II ($h\nu = 40.8$ eV) spectra at emission angles corresponding to $\bar{M}$, which show no discernible dispersion of S_2 with wave vector perpendicular to the surface. The sensitivity of S_2 to adsorption also illustrates its surface character, being strongly suppressed by exposure to oxygen and CO. In the case of both adsorbates, S_2 appears to be more reactive than the S_1 Tamm state. At $h\nu = 21.2$ eV, $\bar{M}$ for S_2 corresponds to an emission angle of 62.5°. At this point, S_2 lies at 2.113-eV binding energy with an experimental FWHM of 30 meV, which, allowing for instrumental broadening, corresponds to an inverse lifetime of 25 meV. Although a polarized photon source was not available in the present study, previous work by Westphal and Goldmann[8] can be used to deduce the orbital symmetry of S_2. In their spectra B_1 and S_2 are not resolved (see Fig. 1 in Ref. 8) but the data clearly show that both B_1 and S_2 have odd parity in the ΓXWK mirror plane. This rules out the assignment of S_2 at $\bar{M}$ to an $\bar{M}_4$ Tamm state, which has a mainly $d_{3z^2-r^2}$ basis and is predicted by Smith, Gay, and Arlinghaus[12] to lie 90 meV below, and by Euceda and co-workers[13] to lie about 55 meV below the top of the $\bar{M}_{2,3}$ continuum. The third predicted Tamm state does have odd parity, consisting of d_{xy} orbitals localized in the subsurface plane. However, this $\bar{M}_3$ state should lie 30 meV (Ref. 13) to 142 meV (Ref. 12) above the $\bar{M}_{2,3}$ continuum, which is not consistent with the experimental data, and the reactivity of S_2 to adsorbates would be surprising if it derived from subsurface orbitals. Hence, the slab calculations do not give a satisfactory explanation for the origin of S_2. This can only be achieved by consideration of relativistic effects on the bulk electronic structure.

The dispersion of S_2 along Σ in the surface Brillouin zone is shown in Fig. 3 along with the surface projection of a bulk band structure obtained from a recent relativistic calculation.[15] This shows clearly that S_2 exists in a spin-orbit-induced absolute band gap which extends one-third the length of $\bar{\Sigma}$ from $\bar{M}$. A surface projection of the nonrelativistic band structure does not give rise to a gap in this region.[18] The origin of the spin-orbit gap can be seen most clearly at $\bar{M}$, which corresponds to the Z line in the bulk zone. Here, spin-orbit coupling splits the X_5 band into 7^+ and 6^+ components, separated by 150 meV,[15] opening a gap between the $\bar{M}_{2,3}$ and $\bar{M}_5$ continua (using nonrelativistic labels). Away from $\bar{M}$, along $\bar{\Sigma}$, the gap is extended by spin-orbit mixing and repulsion of the top three d bands.

The orbital bases for the nonrelativistic, surface-projected $\bar{M}$ bulk continua and their Z-band origins are shown in Table I. The continuum basis sets are separated into B and A (001) planes which have axes identical in z but with x and y rotated 45° to each other.[13,14,18] The axes used for the surface (B) plane in Table I are those shown in Fig. 1. Spin-orbit coupling mixes the basis functions shown in Table I, although for copper this effect should be small at

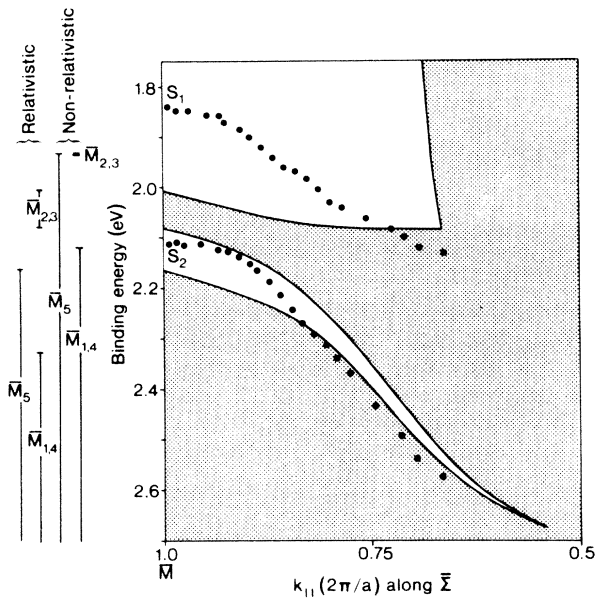

FIG. 3. Experimental dispersion relations for the surface states S_1 and S_2 along with the projected relativistic bulk band structure from Ref. 15. The $\bar{M}$ continua for the relativistic (Ref. 15) and nonrelativistic (Ref. 17) band structures are indicated.

points away from where band crossing would occur in the nonrelativistic scheme. Hence, the symmetry labels and associated basis functions in Table I are still of value. At $\bar{M}$, the continua separated by the spin-orbit gap have odd parity ($\bar{M}_{2,3}$), and mixed parity ($\bar{M}_5$) bases with respect to the ΓXWK mirror plane. The experimentally determined odd parity of S_2 therefore provides compelling evidence that it is a hybridized Shockley state. This result is not surprising in that there is considerable theoretical support for the existence of such a state within a spin-orbit gap.[19,20]

The existence of the $\bar{M}_2$ Tamm state can be explained in the absence of relativistic effects. However, its observed binding-energy separation from the d-band maximum is 350 meV lower than theoretically predicted.[12] The currently favored explanation for this discrepancy involves a difference in the relaxation energy of a bulk and surface state

TABLE I. The basis functions (for axes in Fig. 1) in the nonrelativistic scheme for Cu(001) $\bar{M}$ continua and their band origins. The surface plane is type B; the subsurface plane is type A.

Bulk bands	Surface-projected bulk continua	Basis functions B plane	Basis functions A plane
Z_1	$\bar{M}_1$	$d_{x^2-y^2}$	$d_{3z^2-r^2}$
	$\bar{M}_4$	$d_{3z^2-r^2}$	$d_{x^2-y^2}$
Z_2	$\bar{M}_2$	d_{xy}	. . .
	$\bar{M}_3$	. . .	d_{xy}
Z_3, Z_4	$\bar{M}_5$	d_{xz}, d_{yz}	d_{xz}, d_{yz}

photohole. The relaxation energy of a bulk $3s$ core hole has been predicted to be 300 meV larger than that for a corresponding surface core hole.[21] This figure, assuming its transference to d-band holes,[22] would explain the experimental binding energy of the $\bar{M}_2$ state, although some doubt has been expressed regarding the magnitude of the relaxation shift.[7] Relativistic effects alone would increase the calculated Tamm state binding energy of $\bar{M}_2$ simply by introducing orbitals other than d_{xy} into the $\bar{M}_2$ basis. This would reduce the marked localization of $\bar{M}_2$ in the surface plane and hence its energy separation from the $\bar{M}_{2,3}$ continuum. The corresponding effect on the bulk states can be observed as a broadening of the calculated $\bar{M}_{2,3}$ continuum, as shown in Fig. 3.

It is likely that, in general, the electronic structure and reactivity of a first-row transition-metal surface will be significantly influenced by relativistic effects, *via* subtle changes to the bulk electronic structure. However, as in the example described above, the unambiguous identification of such effects by ARP will be difficult, even in the case of copper, where lifetime broadening of the spectra is minimized.

We are grateful to F. J. Arlinghaus and J. Noffke for providing unpublished data from their calculations. We also thank H. A. Padmore for the loan of the Cu(001) crystal used in the work and B. Pearce for his assistance in recording the data. This work was supported by the Science and Engineering Research Council (U.K.). Additional support was received from the United Kingdom Atomic Energy Authority and Vacuum Science Workshop Ltd.

*Present address: Science and Engineering Research Council, Daresbury Laboratory, Warrington WA4 4AD, U.K.
†To whom correspondence should be addressed.

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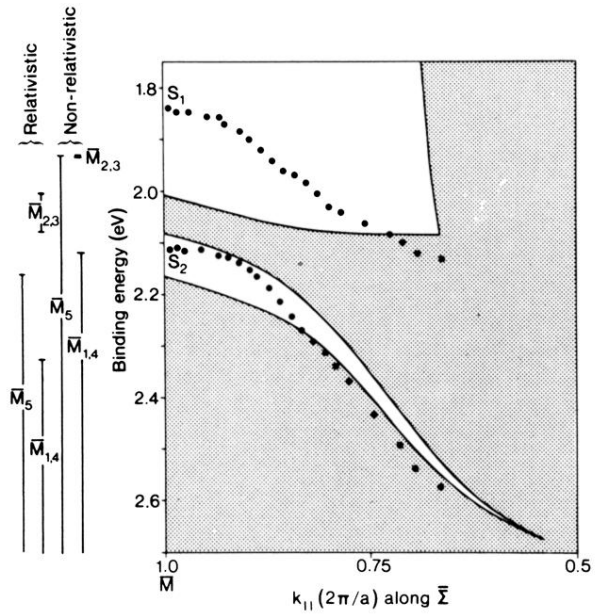

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