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Observation of new surface states on Cu(110) with the use of angle-resolved photoelectron spectroscopy

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Angle-resolved photoemission investigations of the Cu(110) surface reveal the existence of surface states along the $\bar{\Sigma}$ line of the two-dimensional Brillouin zone. Midway between the $\bar{\Gamma}$ and $\bar{X}$ symmetry points they are located above the tops of the $\bar{\Sigma}_1$ and $\bar{\Sigma}_2$ symmetry subbands of the occupied d states and run out of the gaps on the way to $\bar{\Gamma}$ and $\bar{X}$, respectively, and become resonances. Their band dispersions and symmetry characters have been measured, and are compared with a second-principles, fully relativistic calculation of the bulk continuum. The observed surface states are not predicted by existing calculations of the surface electronic structure.

In this Rapid Communication we report the first observation of electronic d-band surface states (SS) on Cu(110) employing angle-resolved ultraviolet photoelectron spectroscopy (ARUPS). Over the past decade, copper has provided an ideal testing case for comparisons between ARUPS studies and first-principles calculations of bulk and surface electronic structure.[1,2] Numerous SS dispersions have been measured. An *sp* SS band exists just below the Fermi surface in the center of the two-dimensional surface Brillouin zone (2D BZ) of the (111) surface.[3,4] This Shockley-type SS is a general property of the $L_{2'}$-L_1 gap of the 3D BZ and also occurs on Cu(110) ($\bar{Y}$ symmetry point) and on (111) and (110) faces of Ag and Au.[5,6] Further, a *sp* SS band located near the Fermi energy at the $\bar{X}$ point of the Cu(001) surface has been measured.[7] Surface states with d-character split off from the upper edge of the 3D d-band continuum (Tamm states) have been observed at the $\bar{M}$ point of the 2D BZ's of (001) and (111) surfaces of the noble metals.[8,9] These above mentioned SS occur in absolute gaps of the bulk band structure projected onto the surface (PBBS) and are in semiquantitative agreement with calculated results.[10–14]

The surface states reported in this Rapid Communication are located in gaps of the symmetry resolved d-band PBBS between $\frac{1}{4}$ and $\frac{3}{4}$ of the way along $\bar{\Sigma}$ between the $\bar{\Gamma}$ and $\bar{X}$ symmetry points of the 2D BZ of Cu(110). They become resonances around $\bar{\Gamma}$ and $\bar{X}$ and are split off from the upper edges of the $\bar{\Sigma}_1$ and $\bar{\Sigma}_2$ d subbands, respectively.

Experiments were performed in an ARUPS spectrometer described elsewhere.[6] Energy resolution was about 80 meV and angular resolution was 3°, both full width at half maximum. The Cu(110) crystal was the same as that used previously[6] and was cleaned by cycles of Ar-ion sputtering and annealing, yielding sharp low-energy electron diffraction spots. The crystal sample was aligned by low-energy electron diffraction (LEED) and by a measurement of the dispersion of the L-gap surface state at $\bar{Y}$ along $\bar{\Delta}$. Rare-gas resonance radiation (He I and He II, Ar I, and Ne I) was incident at 50° from the surface normal in the (001) mirror plane. The electron momentum parallel to the surface, $\vec{K}_{\parallel}$, was varied by rotating the energy analyzer in that plane (ΓKWX plane in 3D $\vec{k}$ space).

Some typical AREDC's taken with unpolarized He I radiation are shown in Fig. 1 for both the clean and the oxygen exposed surfaces. Also shown are the difference spectra.

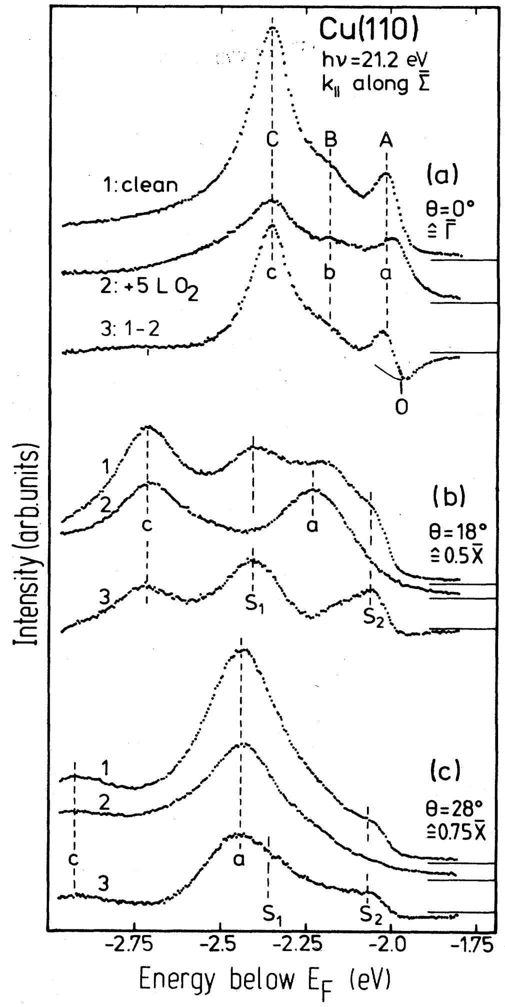

FIG. 1. Angle-resolved energy distribution curves (AREDC's) taken at $h\nu = 21.2$ eV from Cu(110) along the $\bar{\Sigma}$ line at $\bar{\Gamma}$ (top), at about $0.5\bar{X}$ (middle), and at about $0.75\bar{X}$ (bottom). The spectra denoted with 1 are from the clean surface, the AREDC's 2 represent the spectra after exposure of 5 L O_2 (1 L $= 10^{-6}$ Torr sec), the AREDC's 3 are the difference spectra 1-2. S_1 and S_2 are the surface-state emissions; A, B, and C and a, b, and c denote the bulk emissions from the clean and the contaminated surface, respectively, whereas 0 is an emission from adsorbed oxygen.

The surface-state emissions S_1 and S_2 are best resolved at external photoelectron polar angles around $\theta = 18°$ corresponding to $K_{\parallel} \simeq 0.5\overline{\Gamma}\overline{X}$. They are totally quenched by adsorption of half a monolayer of atomic oxygen [indicated by the occurrence of the well-known (2×1) LEED pattern]. The surface-state emissions are also suppressed by the adsorption of atomic hydrogen.[15] The emissions A, B, and C, and a, b, and c are bulk emissions of the clean- and oxgyen-covered surface, respectively. At $\theta = 0° (K_{\parallel} = 0, \overline{\Gamma})$ the surface-state emissions coincide with the bulk emissions $A-C$, the former thus being surface resonances. At $\theta \gtrsim 28° (K_{\parallel} \gtrsim 0.75\overline{\Gamma}\overline{X})$ the surface state S_1 is superimposed by the bulk emission A and is scarcely to detect. The surface states S_1 and S_2 have also been detected with Ar I, Ne I, and He II radiation. Because the SS do not occur in absolute gaps of the PBBS, bulk and SS emissions overlap in certain polar angle regions. The SS dispersions measured with the different photon energies are identical in those $K_{\parallel}$ regions where the SS emissions could be separated unambigously from the bulk emissions (Ne I: $0 \leq K_{\parallel} \leq 0.75\overline{\Gamma}\overline{X}$; Ar I: $0 \leq K_{\parallel} \lesssim 0.5\overline{\Gamma}\overline{X}$; He II: $K_{\parallel} = 0, 0.5\overline{\Gamma}\overline{X}, 1.0\overline{\Gamma}\overline{X}$). Thus, the necessary condition of the $k_{\perp}$ independence of the dispersion is fulfilled in the photon energy range 12 eV $\lesssim h\nu \lesssim 41$ eV. The origin of both the bulk and surface emissions will be discussed below.

Figure 2 shows the relativistic bulk band structure of Cu [spin-orbit (so) interaction included] along lines in $\vec{k}$ space perpendicular to the (110) surface in the ΓKWX plane. The calculation has been performed with the second-principles interpolation scheme of Smith and Mattheiss[16] using a parameter set fitted to the experimental bulk band structure.[2,17] The calculation has been done for the $K_{\parallel}$ values given in the figure in the range $0 \leq K_{\perp} \leq 2^{1/2}$ [$K_{\perp}$ in units of $(2\pi/a)$], thus giving all bulk bands along these lines. The bands indicated by dashed lines have odd parity under reflection through the (001) mirror plane. This, of course, is an approximation because the so interaction does not only lift degeneracy but mixes bands of different parity. Sohn, Dempsey, Kleinman, and Caruthers (SDKC) (Ref. 18) have performed a tight-binding calculation of energy bands for a 47 layer (110) copper thin film using parameters obtained by fitting to Burdick's[19] bulk band calculation. Apart from so interaction, which is not included in Burdick's calculation, our second-principles calculation (Fig. 2) is in good agreement with Burdick's result and with a recent fully relativistic calculation based on local-density functional theory.[20] SDKC have reported results obtained both with and without a shift of the zeroth-neighbor parameters on the surface planes.

For the discussion of the PBBS we use the shown energy dispersions including so coupling but the nonrelativistic symmetry classification. Three absolute gaps along $\overline{\Sigma}$ exist, indicated by the horizontally hatched regions in Fig. 2, the gap at about -3.7 eV extending a longer way from $\overline{X}$ to $\overline{\Gamma}$ as compared to the nonrelativistic calculation of SDKC because of the lifting of degeneracy by the so interaction. The subbands span three $\overline{\Sigma}_1$ gaps (even-parity bands) and one $\overline{\Sigma}_2$ gap (odd-parity bands) marked by the diagonally hatched regions. According to the calculation of SDKC the two absolute gaps are empty, whereas one $\overline{\Sigma}_1$ SS in each of the two lower $\overline{\Sigma}_1$ gaps and one $\overline{\Sigma}_2$ SS in the $\overline{\Sigma}_2$ gap are predicted. The energetic positions of the SS are indicated by the arrows in Fig. 2.

Cu(110)/ΓKWX spectra have already been published[2,21-24] and discussed in terms of light polarization selection rules (PSR) (Refs. 21, 23, and 24) and final-state gap emission.[2,21,22] The structures A, B, and C in the clean-surface spectra and equivalently the structures a, b, and c in the contaminated-surface spectra shown in Fig. 1 are direct transitions from the upper three d bands located in the second 3D BZ on constant energy difference curves $(\Delta E = h\nu = E_f - E_i)$ close to the 3D Σ line parallel to the surface which intersects the surface normal $(\Gamma_{000} - \Sigma - X_{110}$ direction in 3D $\vec{k}$ space) in the X_{110} symmetry point $(K_{\parallel} = 0, K_{\perp} = 2^{1/2})$. This has been found by using the triangulation method in comparing the dispersions of the structures in the Cu(110)/ΓKWX-AREDC's with those in Cu(001)/ΓXWK-AREDC's. Further, the He I and Ne I derived dispersions of the bulk structures with $K_{\parallel}$ are identical up to $K_{\parallel} \simeq 0.5\overline{\Gamma}\overline{X}$. The extended-zone wave vectors of the direct transitions thus have perpendicular components $K_{\perp} \simeq 2^{1/2}$ (Ref. 25) in the shown $K_{\parallel}$ region (see Figs. 1 and 2). Owing to the nonrelativistic PSR the structure (A,a) is seen with s-polarized light (initial band with

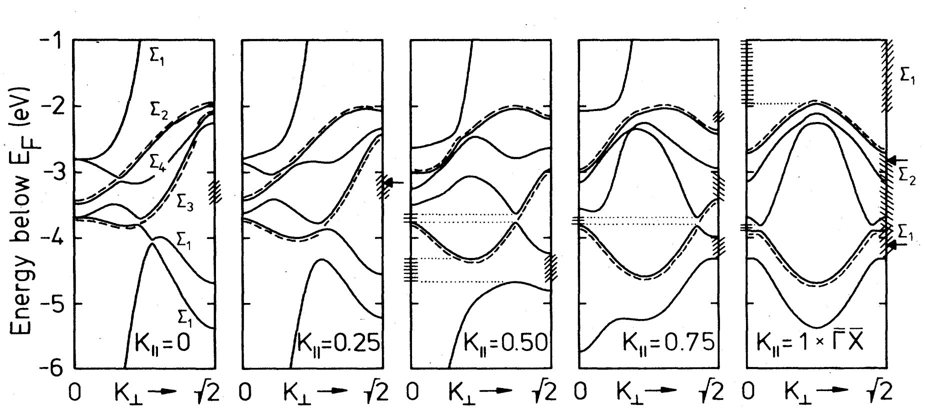

FIG. 2. Occupied band structure of Cu along straight lines perpendicular to the (110) surface in the ΓKWX plane. The $K_{\parallel}$ values and the $K_{\perp}$ region [given in units of $(2\pi/a)$] are indicated. The dashed lines indicate the bands with odd parity under reflection through the ΓKWX plane if the parity mixing due to spin-orbit interaction is neglected. The single group symmetry labels of the bands along the Σ line $(K_{\parallel} = 0)$ is also given. The hatched areas indicate the absolute and subband gaps discussed in the text, the arrows give the energetic positions of surface states as predicted in Ref. 18.

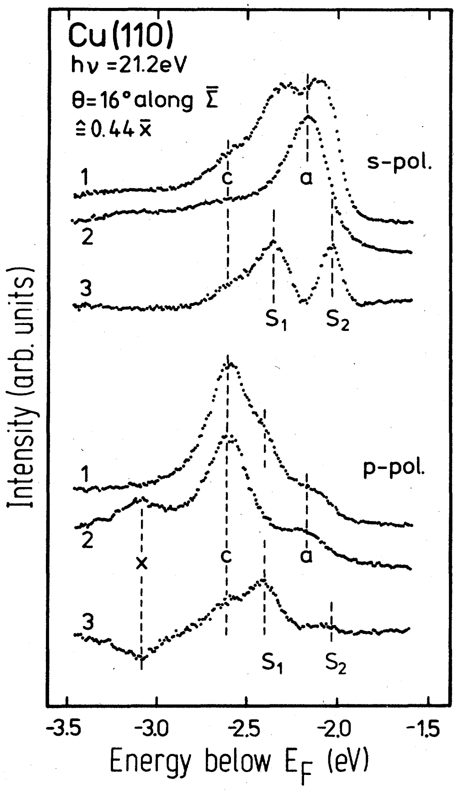

FIG. 3. AREDC's at $K_{\parallel} \simeq 0.44\bar{\Gamma}\bar{X}$ taken with *s* polarized (incident light polarization perpendicular to the ΓKWX mirror plane, top) and *p* polarized (polarization in the ΓKWX plane, bottom) He I radiation from the clean (1) and the contaminated (2) surface, respectively. The spectra 3 give the difference spectra.

odd symmetry Σ_2) for $K_{\parallel} \neq 0$, whereas the corresponding transition is forbidden for $K_{\parallel}=0$. Structure (C,c) is seen with *p*-polarized light (Σ_4 symmetry). The transition strength for structure (B,b) is so small that it is resolvable only for small $K_{\parallel}$. The nonrelativistic PSR are, of course, somewhat relaxed due to the so interaction.[24] This is confirmed by our measurements. The symmetry character of the SS is best seen at $K_{\parallel} \simeq 0.50$ (Fig. 3), where the SS emissions are energetically well separated from the bulk emissions. S_2 has odd symmetry like the bulk emission (A,a) and thus corresponds to the $\bar{\Sigma}_2$ subbands. S_1 corresponds in nonrelativistic approximation to the Σ_1 subbands, and is seen both in *s* and *p* polarization because of the so interaction induced mixing of the symmetries. This can be understood by an inspection of Fig. 2. The upper edge of the $\bar{\Sigma}_2$ subbands is energetically well separated from the $\bar{\Sigma}_1$ bands, whereas the upper edge of the $\bar{\Sigma}_1$ bands is in neighborhood to $\bar{\Sigma}_2$ bands so that the relativistic mixing is strongest for S_2. This interpretation is confirmed by a comparison of the experimental dispersions of S_1 and S_2 with the symmetry resolved projected bulk continua as obtained from our second-principles calculation (Fig. 4). At $\bar{\Gamma}$ the energies of the bulk emissions should coincide with the calculated *d*-band energies at $\bar{X}$;[25] therefore, the theoretical energies

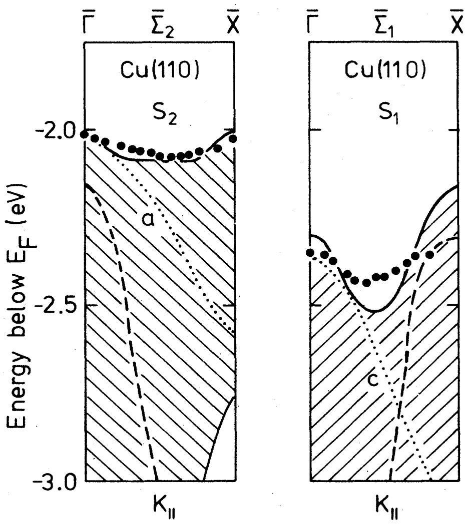

FIG. 4. Surface-state dispersions (●) and projected bulk continua with $\bar{\Sigma}_2$ and $\bar{\Sigma}_1$ symmetry, respectively (hatched regions). The latter have been calculated using the relativistic version of the combined interpolation scheme. Also shown are the upper edges of the lower $\bar{\Sigma}_2$ and $\bar{\Sigma}_1$ subbands (dashed lines), and the dispersions of the bulk emissions *a* and *c* (dotted curves).

have been lowered by 50 meV to achieve this coincidence for the emission *a*.

The conclusion from Fig. 4 is that the surface state S_2 splits off from the $\bar{\Sigma}_2$ continuum and runs above the upper edge of the $\bar{\Sigma}_2$ subbands, whereas the surface state S_1 splits off from the $\bar{\Sigma}_1$ continuum. Both surface states run into the upper edges of the corresponding continua on the way to $\bar{\Gamma}$ and $\bar{X}$ and become resonances. No other surface states have been found in our investigation.

In summary, using ARUPS we have found two new surface states on Cu(110) along $\bar{\Sigma}$ split off from the tops of the $\bar{\Sigma}_1$ and $\bar{\Sigma}_2$ *d*-state subbands of the bulk continuum into the gaps above them. These surface states are not predicted by theory,[18] whereas the calculated SS have not been found. Similar SS have been detected on Ag(110), a detailed investigation of the latter will be published elsewhere. New calculations of the electronic structures of Cu(110) and Ag(110) surfaces are recommended. These surfaces are of special interest with regard to the adsorption of oxygen on them and whether adsorption induces surface reconstructions.[26,27] The dispersions of the bulk transitions on both the clean- and oxygen-covered surfaces do not differ by more than the experimental uncertainty of 0.02 eV.[28] Further, the energies of the surface states do not depend on the degree of coverage up to their disappearance at the formation of the ordered oxygen overlayer. Thus, we conclude that the oxygen overlayer potential does not lead to a strong modification of the electronic band structure of the measured substrate layers. Further, a fully relativistic calculation would be helpful in order to clarify whether these new SS are true symmetry SS or whether their existence depends on spin-orbit interaction.

[1] F. J. Himpsel, Adv. Phys. **32**, 1 (1983), and references therein.

[2] R. Courths and S. Hüfner, Phys. Rep. **112**, 53 (1984), and references therein.

[3] P. O. Gartland and B. J. Slagsvold, Phys. Rev. B **12**, 4047 (1975); St. G. Louie, P. Thiry, R. Pinchaux, Y. Petroff, D. Chandesris, and J. Lecante, Phys. Rev. Lett. **44**, 549 (1980); S. A. Lindgren and L. Walldén, Phys. Rev. B **22**, 5967 (1980); S. D. Kevan, Phys. Rev. Lett. **50**, 526 (1983).

[4] P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Surf. Sci. **85**, 263 (1979); S. Kevan, Phys. Rev. B **28**, 4822 (1983).

[5] P. Heimann, H. Neddermeyer, and H. F. Roloff, J. Phys. C **10**, L17 (1977); P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Phys. Rev. Lett. **43**, 1757 (1979); P. Heimann, M. Miosga, and H. Neddermeyer, Solid State Commun. **29**, 463 (1979); Phys. Rev. Lett. **42**, 801 (1979).

[6] R. Courths, H. Wern, U. Hau, B. Cord, V. Bachelier, and S. Hüfner, J. Phys. F **14**, 1559 (1984).

[7] S. D. Kevan, Phys. Rev. B **28**, 2268 (1983).

[8] P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Phys. Rev. Lett. **42**, 1782 (1979); Phys. Rev. B **20**, 3059 (1979); D. Westphal and A. Goldman, Surf. Sci. **95**, L249 (1980); S. D. Kevan and D. A. Shirley, Phys. Rev. B **22**, 542 (1980).

[9] H. Neddermeyer, J. Phys. F **12**, L241 (1982); A. Goldmann and E. Bartels, Surf. Sci. **122**, L629 (1982); P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Phys. Rev. Lett. **43**, 1757 (1979).

[10] J. A. Appelbaum and D. R. Hamann, Solid State Commun. **27**, 881 (1978).

[11] J. G. Gay, J. R. Smith, and F. J. Arlinghaus, Phys. Rev. Lett. **42**, 332 (1979).

[12] D. G. Dempsey and L. Kleinmann, Phys. Rev. B **16**, 5356 (1977).

[13] D. W. Bullet, J. Phys. C **14** 4521 (1981).

[14] A. Euceda, D. M. Bylander, L. Kleinman, and K. Mednick, Phys. Rev. B **27**, 659 (1983).

[15] Hydrogen exposure up to 5×10^3 L (where 1 L$=10^{-6}$ Torr sec) did not quench the intensities of S_1 and S_2 totally. Atomic hydrogen chemisorbs on Cu surfaces at $T\simeq300$ K. Atomic hydrogen was produced by hot W filaments (ion gauge and ion gun), but the efficiency of these methods is low. See F. Greuter and E. W. Plummer, Solid State Commun. **48**, 37 (1983).

[16] N. V. Smith, Phys. Rev. B **19**, 5019 (1979); R. Lässer, N. V. Smith, and R. L. Benbow, *ibid.* **24**, 1895 (1981).

[17] H. Wern, doctoral thesis, Saarbruecken, 1985 (unpublished).

[18] K. S. Sohn, D. G. Dempsey, L. Kleinmann, and E. Caruthers, Phys. Rev. B **14** 3193 (1976).

[19] G. Burdick, Phys. Rev. **129**, 138 (1963).

[20] H. Eckard, L. Fritsche, and J. Noffke, J. Phys. F **14**, 97 (1984).

[21] E. Dietz and F. J. Himpsel, Solid State Commun. **30**, 235 (1979).

[22] R. Courths, Solid State Commun. **40**, 529 (1981).

[23] A. Goldmann, D. Westphal, and R. Courhs, Phys. Rev. B **25**, 2000 (1982).

[24] H. Przybylski, A. Baalmann, G. Borstel, and M. Neumann, Phys. Rev. B **27**, 6669 (1983).

[25] In the $K_{\parallel}$ region around $K_{\parallel}=0$ the term "direct transition" is used for transitions into evanescent final states which fill the gap between the bulk bands 9 and 10 along the Σ line. In the weak damping limit, which is favored by the results, the real part of the wave-vector component $K_{\perp}$ of these gap states is approximately equal to $\Gamma KX=(2\pi/a)2^{1/2}$. For higher $K_{\parallel}$ values the transitions move away from the X_{110}-Σ-Γ_{020} line because bulk transitions are then allowed. A full representation of the location of the bulk transitions in $\vec{k}$ space will be given elsewhere. See also Ref. 2.

[26] U. Döbler, K. Baberschke, J. Haase, and A. Puschmann, Phys. Rev. Lett. **52**, 1437 (1984).

[27] Th. M. Hupkens and J. M. Fluit, Surf. Sci. **143**, 267 (1984).

[28] This is certainly true for transition (C,c). Transition (A,a) fills the gap between S_1 and S_2 at low $K_{\parallel}$ (Fig. 1) and its energy is uncertain by about 0.05 eV.