$\leq e^{-m|j|}$ with $m = \lim_{j\to\infty}(-j)^{-1}\ln[g(j)]$.

[4]B. Simon, to be published.

[5]E. Lieb, to be published.

[6]M. Aizenman and B. Simon, to be published.

[7]In a concrete situation, this was already realized by Krinsky and Emery, Ref. 1.

[8]See Ref. 1.

[9]More precisely, consider all paths from α to γ with links of the allowed type. Consider the part of the path from α until the *first* meeting with the set B. $\langle\cdots\rangle'$ has all interactions occurring in these parts of paths.

[10]R. Griffiths, J. Math. Phys. 10, 1559 (1969).

[11]The normalization is that the difference of successive values be 2. Thus, in (4) we are not able to take the $S\to\infty$ limit and attain spins uniformly distributed in $[-1,1]$. But method (E) does work for such spins.

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[15]It is already known [see B. Simon (J. Stat. Phys., to be published)] that there is no spontaneous magnetization in this case.

[16]Normalized so that at $T = 1$ each pair of nearest neighbors has weight 1 in the Hamiltonian. Using different methods, J. Fröhlich and T. Spencer (private communication) have obtained the same bound.

[17]We emphasize that bounds like (8) and (9) hold independent of *any* hypothesis on the form of the falloff.

[18]J. Glimm and A. Jaffe, Commun. Math. Phys. 51, 1 (1976), and 52, 263 (1977).

[19]Defined so that $\beta_c = \sup\{\beta|$ there is a mass gap at $\beta\}$.

[20]This compares unfavorably with Fisher's bound [M. Fisher, Phys. Rev. 162, 480 (1967)] of $\tanh\beta_c \geq 0.37$ and even with the bound $\tanh\beta_c \geq 0.33$ which is obtained trivially with Fisher's method.

[21]O. McBryan and J. Rosen, Commun. Math. Phys. 51, 97 (1967).

[22]R. L. Dobrushin, unpublished. I am grateful to R. Israel, M. Ainzenman, and J. Bricmont for communicating Dobrushin's results to me.

Periodic Oscillations of the Frequency-Dependent Photoelectric Cross Sections of Surface States: Theory and Experiment

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High-resolution angle-resolved photoemission spectroscopy is employed to study surface states on the Cu(111) surface, with use of synchrotron radiation in the energy range $18 \leq \hbar\omega \leq 120$ eV. The results reveal a novel periodic oscillatory behavior in surface-state emission intensity which leads to identification of additional new surface states. A spectral decomposition theory is proposed to explain the physical origin of the oscillations. It describes the measured intensity profiles and predicts that the oscillations are universal for all surface states.

The purpose of this paper is to report the experimental observation and a theoretical explanation of periodic oscillations as a function of photon energy in the photoelectric cross sections of surface states.

Recently angle-resolved photoemission spectroscopy has been actively employed for direct determination of the energy-band dispersion (E vs $\vec{k}$) of many crystals. These measurements have been done mainly at low photon energies[1]

($\hbar\omega < 35$ eV) yielding in general information only over a part of the Brillouin zone. By increasing the photon energy it is possible to cover one, two, or more Brillouin zones. Furthermore, a reduction in the electron mean free path in the higher-energy range (20–150 eV) leads to a more-surface-dominated photoemission spectra.[2] The first high-energy data were obtained by Stöhr *et al.*[3] An accurate determination of the valence band of copper (110) has been obtained recently along ΓKX by Thiry *et al.*,[4] with use of synchrotron radiation between 15 and 100 eV. All the structures observed were explained in a direct-transition model and no surface states were observed. The situation, however, is found to be quite different for the (111) and (100) faces.

We have measured angle-resolved energy-distribution curves (AREDC) for Cu(111) single crystals using photon energies between 18 and 120 eV. The results allow a determination of E vs $\vec{k}$ along ΓL but this aspect will not be discussed here.[5] We will instead concentrate on the observation of new surface states and on the remarkable oscillatory behavior of their emission intensities. The measurements were performed at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, the Orsay Synchrotron Radiation Center. The use of a toroidal grating monochromator[6] allows us to work with an energy resolution for monochromator and analyzer that varies between 130 meV at low photon energies to 170 meV at 100 eV. The angular resolution is smaller than 1°. The energy-distribution curves were obtained with either s- or p-polarized light, making it possible to draw conclusions about the symmetry of the initial state.[7] The analyzer is a 127° cylindrical one and the count rate for the Cu d bands, with the experimental conditions previously described was of the order of 20 000 counts/sec. The Cu crystals were prepared by argon etching and annealing at 500 °C, the cleanliness of the surface was checked by Auger-electron spectroscopy. The vacuum was less than 2×10^{-10} Torr and no contamination was observed even after several hours.

Figure 1 shows the angle-resolved photoemission spectra, taken at normal emission, for various photon energies. The two structures S_1 and S_3 have the following properties:

(a) They show no dispersion when the photon energy is changed.

(b) They are both excited only with p-polarized light.

(c) They are located in band gaps.

(d) Their intensity decreases very strongly when the sample is exposed to oxygen. This is illustrated in Fig. 2(a) which shows normal-emission ($k_{\parallel} = 0$) angle-resolved photoemission curves obtained at $\hbar\omega = 70$ eV with p-polarized light, for a clean surface and for a coverage of 1200 L of oxygen (1 L = μTorr sec). Figure 2(b) shows the difference between the two curves.

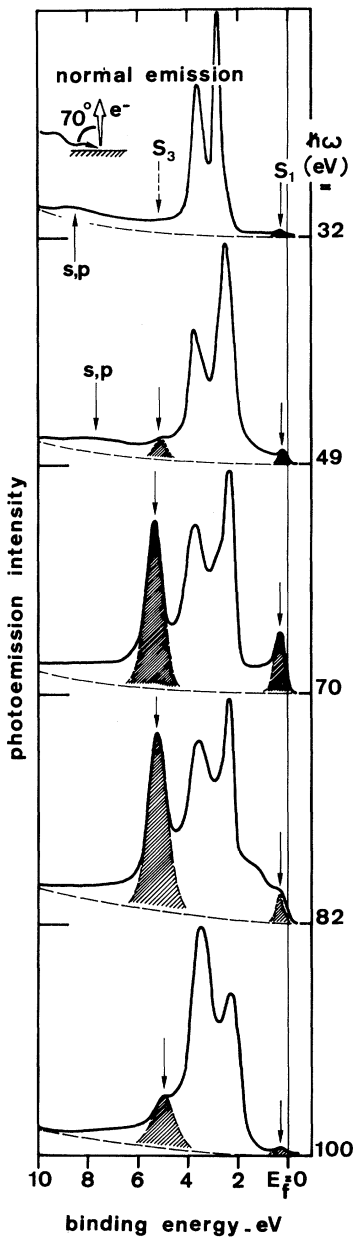

FIG. 1. Normal-emission ($k_{\parallel} = 0$) angle-resolved photoemission distribution curves obtained at various photon energies. S_1 and S_3 are the surface states discussed in the text. The light is p polarized.

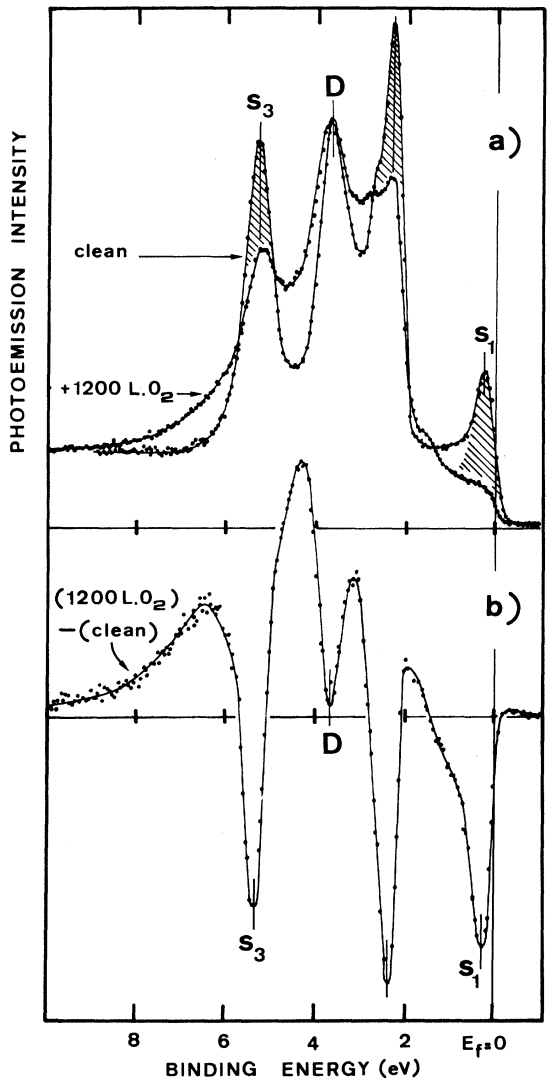

FIG. 2. (a) Normal-emission ($k_\parallel = 0$) angle-resolved photoemissions curves obtained at $\hbar\omega = 70$ eV for Cu(111) with p-polarized light, clean and covered with 1200 L of oxygen. (b) The lower curve is the difference between the two previous curves.

However, we find that some bulk transitions also show high sensitivity to oxygen, and so we do not solely use this criterion to prove that S_1 and S_3 are surface states but rather use it to show the similarity between S_1 and S_3.

(e) The intensities of S_1 and S_3 show the same oscillatory behavior. With use of a free-electron model for the final state, the intensities of S_1 and S_3 as a function of $k_\perp$ (or $\hbar\omega$) are found to have a maximum at the L point (71 eV for S_1, 75 eV for S_3). At lower photon energies the intensity of S_1 increases again as the L point is approached but S_3 is not observed for reasons that are discussed later.

S_1 is a surface state, first identified by Gartland and Slagsvold,[8] lying in the Λ_1-symmetry gap above L_2' and has been also observed in Ni,[9] Ag,[10] and Au.[11] From the similarity of the S_1 and S_3 behavior we conclude that S_3 is also a surface state. Theoretically, a surface state similar to S_3 (both in energy position and symmetry) has been predicted for the Pd(111) surface in a self-consistent calculation.[12]

We propose the following theoretical explanation for the observed oscillations of the photoelectric cross sections. A surface state ψ_s of parallel momentum $k_\parallel$ and energy E_s is decomposed as

$$\psi_s = \sum_{\vec{k}_\perp, n} \alpha_n(\vec{k}_\perp)\varphi_n(\vec{k}_\perp), \tag{1}$$

where φ_n are bulk states of the appropriate $k_\parallel$ in the nth band. In a situation where a direct-transitions picture is valid, conservation of energy implies that a substantial part of the photoemission is into a bulk final state of $k_\perp$ determined by the relation $E(k_\perp) - E_s = \hbar\omega$. The expression for the emission intensity at $\hbar\omega$ in this formulation is

$$I_s(\hbar\omega) \sim |\textstyle\sum_n \alpha_n(\vec{k}_\perp) M_b(n)|^2, \tag{2}$$

where M_b is a transition matrix element for the bulk bands. Hence I_s is oscillatory in $\hbar\omega$ for surface states in general since $|\alpha_n(\vec{k}_\perp)|$ is usually a strongly peaked function of $k_\perp$ and the frequency dependence of the bulk emission intensity I_b is usually smooth especially for s and p states.[13] In particular, if the surface state is primarily derived from a single bulk band [as in the case of the surface states on Cu(111) and other surfaces[12,14]]. I_s/I_b is periodic in $k_\perp$ and has maxima at $\hbar\omega$ corresponding to the $k_\perp$ at which the band extremum is closest to E_s.

To quantify this phenomenon for the S_1 and S_3 surface states, we use a semi-infinite linear-chain model in the one-band tight-binding limit.[15] The model is physically sound since both surface states are mainly derived from single narrow Λ_1 bands along the ΓL direction of the Cu bulk band structure. In this model, a surface state exists provided that the condition[15]

$$\chi = 4|\Delta/W| > 1 \tag{3}$$

is satisfied. Here W is the bandwidth and Δ is the shift in the self-energy of a surface orbital relative to that of the bulk. For orbitals with

"effective" interaction appropriate for the Λ_1 bands, Δ may be taken to be positive, and the band maximum is at the zone edge ($k_\perp = \pi/a$) with a surface state splitting off above the band. It is then straightforward to show from Eq. (2) that the relative surface-state emission intensity normalized to that at the zone edge [corresponding to point L for Cu(111)] is given by

$$\left|\frac{\alpha(k_\perp)}{\alpha(\pi/a)}\right|^2 = \frac{(\chi-1)^2}{1+\chi^2-2\chi\cos(k_\perp a-\pi)}. \quad (4)$$

A comparison of the theoretical results with the experimental intensity profiles is presented in Fig. 3. Because our measurements are not absolute, the I_s were measured relative to the emission intensities from the lower d-like Λ_3 bands (structure D in Fig. 2). The comparison between theory and experiment is, therefore, most appropriate in the higher-energy second zone ($\hbar\omega > 30$ eV) where the ratio between s, p, and d cross sections are relatively constant. Moreover, since the $4p$ cross section compared to the $3d$ cross section increases rapidly toward lower photon energies while the $4s$ cross section does the opposite,[13] the surface emission is greatly enhanced for the S_1 state (mostly p-like) and suppressed for the S_3 state (mostly s-like, d_{z^2}-like) in the first zone as observed experimentally.

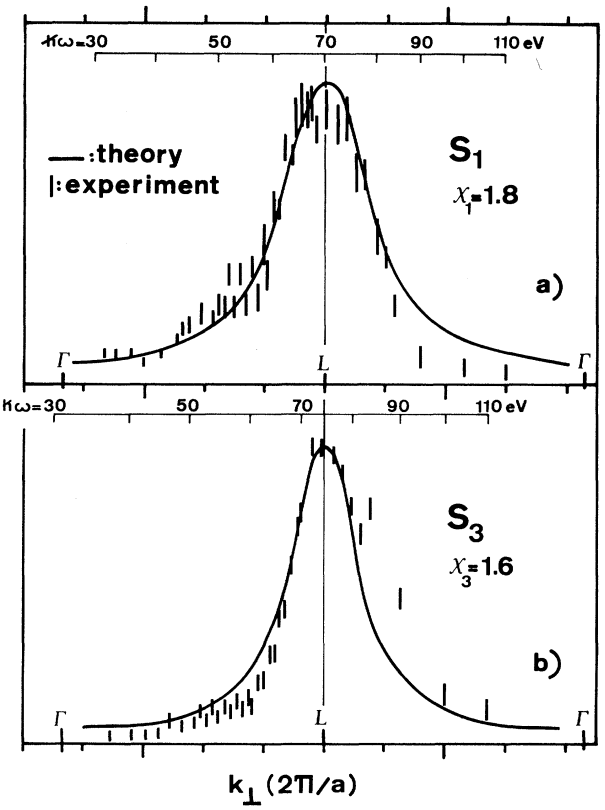

FIG. 3. Variations of the intensities of S_1 and S_3 as function of $k_\perp$. The full line represents the theoretical calculation [Eq. (4)]; the bars are experimental data.

With $\chi_1 = 1.8$ the theory yields an excellent fit for the intensity profile of the S_1 surface state [Fig. 3(a)]. The intensity, as given by Eq. (4), is Lorentzian like near the maximum at $k_\perp = L$ and rapidly dropped to near zero toward Γ. The present analysis should yield a good indication of the surface orbital self-energy shift although the upper Λ_1 band of Cu is not a perfect cosine band. Using an experimental band width of 3 eV, we obtain

$$\Delta = \tfrac{3}{4}(1.8) = 1.35 \text{ eV}, \quad (5)$$

which is a very reasonable value, thus reaffirming the validity of our simple model. Moreover, by keeping the same Δ and scaling χ by the bandwidth, i.e., $\chi_3 = \chi_1 W_1/W_3 = 1.8 \times 3.0/3.4 = 1.6$, we obtain equally excellent agreement with experiment for the S_3 state [Fig. 3(b)].

Thus, with just a single number, the theory accurately describes and correlates the observed resonance energies and emission intensity profiles of both surface states. We anticipate that the oscillations reported here are a general phenomenon which should be observable for other surface states[16] and that they will be useful in determining experimentally the character and origin of surface states.

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ERRATA

X-RAY DETERMINATION OF ANHARMONICITY IN V_3Si. J.-L. Staudenmann and L. R. Testardi [Phys. Rev. Lett. 43, 40 (1979)].

The definition of the parameter α in Table I should be

$$\alpha \equiv (\langle \mu_\perp^2 \rangle - \langle \mu_\parallel^2 \rangle)/\langle \mu_\perp^2 \rangle$$

in agreement with the text. The authors are thankful to Dr. B. Borie for having pointed this out to us.

STRUCTURE-DEPENDENT 4*f*-CORE-LEVEL BINDING ENERGIES FOR SURFACE ATOMS ON Ir(111), Ir(100)-(5×1), AND METASTABLE Ir(100)-(1×1). J. F. van der Veen, F. J. Himpsel, and D. E. Eastman [Phys. Rev. Lett. 44, 189 (1980)].

On page 189, column 1, the last sentence of the first paragraph should read "...and show for the first time that both binding-energy shifts and surface- to bulk-emission intensity ratios give