Fowler, and F. Stern, Rev. Mod. Phys. 54, 437 (1982).
[3]K. R. Atkins, Phys. Rev. 116, 1339 (1959); K. W. Schwarz, Adv. Chem. Phys. 33, 1 (1975).
[4]C. C. Grimes, Surf. Sci. 73, 379 (1978).
[5]A curious effect: Positive charge can accumulate at the liquid surface without the field tip ever being turned on ($\sim 10^5$ charges in several hours)! We believe this is due to cosmic-ray ionization; see W. L. Willis, Los Alamos Report No. LA-DC-7026, 1965 (unpublished).
[6]D. K. Lambert and P. L. Richards, Phys. Rev. B 23, 3282 (1981).
[7]A. L. Fetter, Ann. Phys. (N.Y.) 81, 367 (1973).
[8]K. Mima, H. Ikezi, and A. Hasegawa, Phys. Rev. B 14, 3953 (1976).
[9]C. C. Grimes and G. Adams, Surf. Sci. 58, 292 (1976).
[10]J. Poitrenaud and F. I. B. Williams, Phys. Rev. Lett. 29, 1230 (1972), and 32, 1213 (1974).
[11]J. Landau, S. G. Lipson, L. M. Määttänen, L. S. Balfour, and D. O. Edwards, Phys. Rev. Lett. 45, 31 (1980).
[12]A. F. Andreev and A. Ya. Parshin, Zh. Eksp. Teor. Fiz. 75, 1511 (1978) [Sov. Phys. JETP 48, 763 (1978)].
[13]σ_{ls} must vary at least as $\sigma_{ls} = \sigma_0 - A T^{1+\epsilon}$ with $\epsilon > 0$. Our observation of roughly linear behavior implies that ϵ is small, $\epsilon \sim 0.1$. With such a small ϵ, m^* would not show deviations from linearity (approaching zero slope at $T = 0$) until well below 10 mK.
[14]H. Ikezi, to be published.

Geometry and Electronic Structure of Cl on the Cu{001} Surface

P. H. Citrin, D. R. Hamann, L. F. Mattheiss, and J. E. Rowe
Bell Laboratories, Murray Hill, New Jersey 07094
(Received 11 August 1982)

The atomic geometry of Cu{001}$c(2\times 2)$–Cl has been determined by surface extended x-ray-absorption fine structure to consist of a simple Cl overlayer in fourfold Cu hollows with a (2.37± 0.02)-Å bond length. With use of this geometry, self-consistent electronic structure calculations were performed and compared with angle-resolved photoemission data, giving excellent agreement for the position and dispersion of several Cl-induced surface states and resonances. These results have resolved previously reported discrepancies for the Ag{001}$c(2\times 2)$–Cl system.

PACS numbers: 68.20.+t, 73.20.Hb, 78.70.Dm, 79.60.Gs

The relationship between geometric and electronic structure at surfaces has been an important theme of modern surface physics. In a recent study, the electronic structure of a half-monolayer of Cl adsorbed on the Ag{001} surface with centered (2 × 2) periodicity was computed for two geometric models, a simple overlayer model (SOM) with Cl occupying fourfold hollow sites and a mixed-layer model (MLM) resembling an epitaxial AgCl{001} plane.[1,2] Comparison with ultraviolet photoemission spectra[3] indicated that the MLM gave the best agreement. In contrast, a study of low-energy electron-diffraction (LEED) intensity spectra showed better agreement with theoretical intensities based on an SOM rather than an MLM.[4] The present study was motivated by this apparent contradiction between two widely used techniques of surface science.

The Cu{001}$c(2\times 2)$–Cl system was chosen as the closest analog to Ag{001}$c(2\times 2)$–Cl which we could presently study with the desired methods. Its geometrical structure was first determined by surface extended x-ray-absorption fine structure (SEXAFS),[5] a technique capable of discriminating between SOM and MLM geometries and of measuring highly accurate bond lengths. The exact geometry was then used as input to a self-consistent electronic structure calculation, which was carried out with sufficient resolution to permit comparison with angle-resolved photoemission spectra. (This degree of detail had not been attempted in the Cl-on-Ag study.) Finally, angle-resolved spectra were measured for a surface prepared exactly as in the SEXAFS measurement. Excellent agreement was obtained between peaks in the calculated and measured spectra, thereby establishing the soundness and consistency of our procedures. The bonding in the Cu{001}$c(2\times 2)$–Cl system ultimately indicated modifications of the SOM geometry used in the initial electronic structure calculations of the Ag{001}$c(2\times 2)$–Cl system and these modifications have resolved the essential contradiction.[1-4]

In the SEXAFS experiment, performed at the Stanford Synchrotron Radiation Laboratory, a clean Cu{001} surface was exposed to 15 ±5 lang-

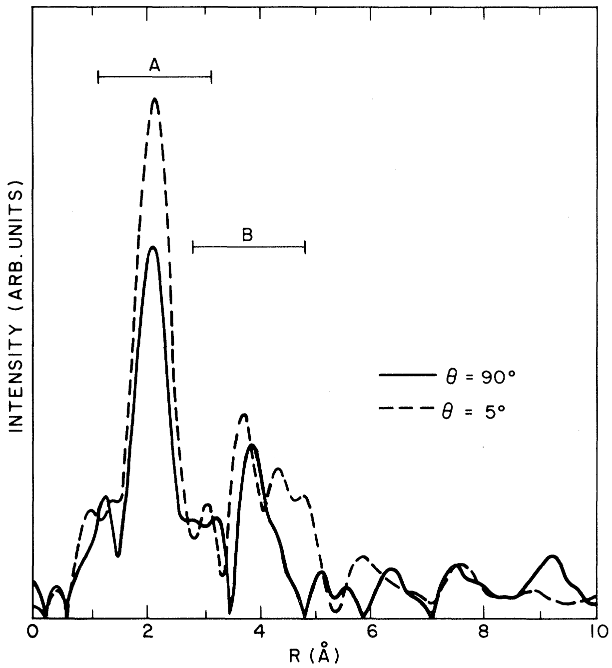

FIG. 1. SEXAFS data Fourier transformed into real space for the two polarizations studied. The lines A and B denote the position and width of the window functions used in back transforming the data to extract the two dominant distances.

muirs (1 langmuir = 10^{-6} Torr sec) of Cl_2 at room temperature and annealed at ~100 °C for 2 min, yielding a sharp $c(2\times 2)$ LEED pattern with low background. SEXAFS signals from the Cl K edge were observed in the range[6] 2800 to 3250 eV with use of the Cl $KLL(^1D)$ Auger line to monitor the absorption rate.[5] The SEXAFS data were taken at polarizations parallel ($\theta = 90°$) and nearly perpendicular ($\theta = 5°$) to the surface.[7] Analysis procedures have been fully discussed elsewhere.[5,7,8] Briefly, the data are normalized to the edge jump, a smooth background is subtracted, and the result is Fourier transformed into real space and shown in Fig. 1. A filter function is placed at position A or B corresponding to the dominant distances in the transform, and the product is back transformed to photoelectron momentum space. This is then compared with identically analyzed EXAFS data from the bulk reference system CuCl. The established principle of phase-shift transferability[8,9] then allows the determination of the surface Cu-Cl distances. We find distances of 2.37 ±0.02 Å and 4.31 ±0.04 Å for $\theta = 90°$, and 2.37 ±0.02 Å and 4.26 ±0.05 Å for $\theta = 5°$.

The polarization dependence of the SEXAFS amplitude $A(k)$ for a given shell of neighbors is particularly simple for K edges,[8] i.e.,

$$A(k) \propto N_S = 3\sum_i |\vec{\epsilon}\cdot\hat{r}_i|^2,$$

where N_S is the effective surface coordination number, $\vec{r}_i$ is the position of the ith neighbor in the coordination sphere, and $\vec{\epsilon}$ is the polarization. Calculated values of N_S are given in Table I for simple overlayer models with atop, bridge, and hollow sites, and for a coplanar mixed-layer model.[1,2] These numbers for both polarizations and their ratios are compared with the experimental values normalized to the reference compound. The mixed-layer model, as well as the atop and bridge geometries, is clearly ruled out, whereas the simple overlayer fourfold hollow site gives typical agreement for the absolute amplitudes and excellent agreement for their ratios. In addition to amplitude considerations, a mixed-layer geometry would be expected to have slightly different distances from the Cl to its two sets of inequivalent Cu neighbors. This would produce an apparent polarization dependence of the measured distance (a weighted average), which is ruled out with high precision by the present results. Finally the fourfold site with the measured nearest-neighbor distance of 2.37 Å leads to a calculated distance of 4.32 Å between Cl and the eight fourth-nearest-neighbor surface Cu atoms, in excellent agreement with the measured values.[10]

With this geometry, the electronic structure was calculated for a five-layer slab (three Cu and two Cl layers). This was done self-consistently within the local density approximation for exchange and correlation by the surface linear augmented plane-wave method[11] (SLAPW) with a completely general potential.[2,12] With this relatively thin slab the Cl density of states is sufficiently accurate for comparison with angle-integrated spectra; a thicker slab, however, is needed to identify surface states and resonances with suf-

TABLE I. Calculated vs experimental N_S values for Cl on Cu{001}.

θ	Onefold atop	Twofold bridge	Fourfold hollow	Mixed layer[a]	Expt.
5°	3.0	4.2	5.0	6.0	4.3 ± 0.8
90°	0	0.9	3.5	9.0	3.1 ± 0.6
5°/90°	∞	4.7	1.4	0.7	1.4 ± 0.2[b]

[a] Calculated with the assumption of all Cu-Cl bond lengths equal to $a_0/\sqrt{2}$.

[b] Determined without reference to model compound, thus explaining smaller experimental uncertainty.

ficient accuracy for comparison with angle-resolved spectra.[13]

Self-consistent results for a thick slab can be simulated with high accuracy by "stretching", i.e., sandwiching the self-consistent bulk potential between surface-region potentials derived from thin-slab calculations.[14] In an alternative version of this approach employed here, a nonorthogonal tight binding (NTB) scheme was fitted to bulk Cu linear augmented plane-wave (LAPW) results. Using nine (s, p, d) functions per atom and first- and second-neighbor two-center Hamiltonian and overlap fitting parameters, a 4-mRy fit was achieved at 21 $\vec{k}$ points. The Cl-Cu interaction parameters were determined from an analogous fit to bulk CuCl LAPW results. With these as a starting point, the fit to the five-layer-slab SLAPW results was systematically improved by successively relaxing surface orbital energies, surface region interactions, and adding allowed crystal-field terms. The mean error of 28 mRy at the start was reduced to 6 mRy in the relaxed fit. Surface NTB parameters from this slab fit were then combined with bulk parameters to generate a "stretched" NTB model for an 11-layer slab.

Cl-induced surface states and resonances are identified by their weight on the Cl adlayer. Those states with weight ≥ 0.15 are plotted in Fig. 2 as solid lines and as hatched areas (indicating resonance width) along the $\bar{\Delta}$ and $\bar{\Sigma}$ symmetry lines in the surface Brillouin zone. These lines lie in reflection planes, and states of even and odd symmetry are plotted separately. The symmetry of the Cl s and p orbitals contributing to these states is indicated. Those in the range -7 to -4 eV form bonding combinations with surface Cu s and d orbitals of appropriate symmetry. Some of the corresponding antibonding combinations form identifiable resonances around -2 eV and $+3$ to $+4$ eV.

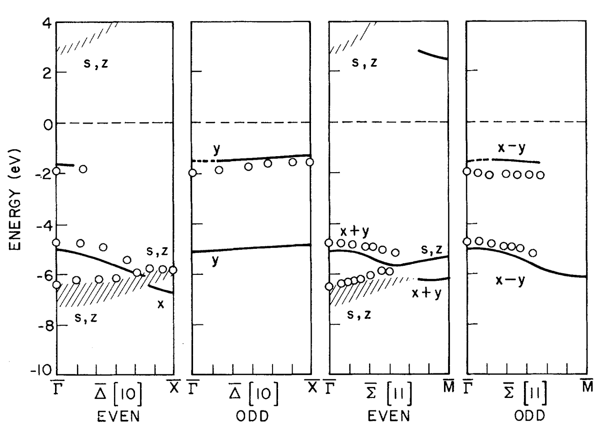

FIG. 2. Cl-induced surface states and resonances from theory (solid lines and crosshatching) and present experiments (open circles) along symmetry lines in surface Brillouin zone, indicating dominant Cl s and p orbital character.

With use of resonance lamp radiation at 16.8 and 21.2 eV, angle-resolved photoemission data were taken on a surface prepared identically as in the SEXAFS experiment. The photoelectrons were energy analyzed in a spherical-grid analyzer, and angle-resolved data were collected with a Vidicon system from a fluorescent screen.[3] Data were collected over a solid angle of 1.1 sr $(70° \times 70°)$ with an angular resolution of $\pm 1.5°$ at 0.5-eV intervals. Spectra of the Cl-covered surface and differences between these and the clean Cu surface were obtained at a series of angles along the $\bar{\Delta}$ and $\bar{\Sigma}$ lines to identify Cl-induced features. The energies of these features are plotted as open circles with the theoretical results in Fig. 2. Since unpolarized light was used, even and odd symmetry cannot be distinguished, and the data are divided between the even and odd plots as suggested by the theory.

The experimental band starting at -2 eV at $\bar{\Gamma}$, also reported by Westphal and Goldmann,[15] is clearly identified with the antibonding p_x, p_y states and is ~0.4 eV lower than the theoretical results. This discrepancy may be traced to the misplacement of the d bands relative to E_F in the LAPW (and other[16]) bulk Cu results. The small dispersion of these bands is given correctly. On the basis of its downward dispersion along $\bar{\Delta}$, the band starting at -4.8 eV is identified as the even p_x band and not the odd p_y band. The corresponding band along $\bar{\Sigma}$ could be either the even $p_x + p_y$ or odd $p_x - p_y$ states and is shown on both plots. The s, p_z resonance starting at -6.5 eV at $\bar{\Gamma}$ is noticeably broader than the other features in the experimental data. The dispersion of these bands is in good agreement with theory, and their absolute position is a few tenths of an electron-volt high. The corresponding bands in Ref. 15 lie a few tenths below the theoretical results, consistent with the d-band shift discussed above. The discrepancy in the two experimental placements is most likely a result of the differing energy resolution combined with the subtraction of a large sloping background in this energy range. The odd bonding p_y band along $\bar{\Delta}$ is not resolved in the present experiment, but the energy distribution curves of Westphal and Goldmann show a weak feature consistent with it.[15]

The present detailed agreement between theory and experiment for Cl-Cu makes implausible an explanation of the Cl-Ag contradiction based on a breakdown of the theoretical electronic structure methods. Recent He-atom-beam-diffraction results for Cl on Ag imply a strongly corrugated surface, consistent with the calculated charge densities for either the Cl-Ag or Cl-Cu simple overlayers but not with the Cl-Ag mixed layer.[17] We now show that this observation, when combined with the present results, indicates that the solution to the initial Cl-Ag problem is a *modified* simple overlayer geometry.

The calculation[1] of the overlayer geometry which had produced results in disagreement with the photoemission data was performed with the bulk AgCl bond length, 2.77 Å, somewhat larger than the best-fit LEED result[4] of $2.67^{+0.03}_{-0.10}$ Å. If, however, we use the present and more precise SEXAFS Cu-Cl surface bond length minus the Cu metallic radius ($a_0/\sqrt{2}$) to define a "surface radius" for Cl, we conclude that the Cl-Ag surface bond should be 0.24 Å shorter than that used in Ref. 1, moving the Cl plane 0.38 Å closer to the Ag surface. This significant change implies much more covalent bonding for fourfold coordinated Cl on the Ag{001} surface than for sixfold coordinated Cl in bulk AgCl. The modified geometry has an interplanar spacing of 1.50 Å, just slightly smaller than the lower limit of the quoted LEED uncertainty range, 1.57 Å.[4] To test the viability of this proposed geometry a calculation of the electronic structure was carried out[18] using that geometry and the methods of Hamann, Mattheiss, and Greenside.[2] Good agreement between the calculated Cl local density of states and the angle-integrated photoemission data[3] was obtained, thus supporting a shorter Cl-Ag bond length and resolving the essential discrepancy which motivated this study. A more precise determination of the Cl-Ag geometry should be possible by SEXAFS with total-yield signal detection[19] and is highly desirable to refine further the electronic structure.

In summary, the most current experimental and theoretical techniques for obtaining detailed geometric and electronic structural information have been used to characterize the Cl-on-Cu{001} system and to resolve a problem of Cl on Ag{001}. The present study demonstrates, in general, the success of such a unified approach in studying chemisorption systems.

The work done at Stanford Synchroton Radiation Laboratory was supported by the National Science Foundation through the division of Materials Research.

[1]H. S. Greenside and D. R. Hamann, Phys. Rev. B 23, 4879 (1981).

[2]D. R. Hamann, L. F. Mattheiss, and H. S. Greenside, Phys. Rev. B 24, 6151 (1981).

[3]S. P. Weeks and J. E. Rowe, J. Vac. Sci. Technol. 16, 470 (1979), and Solid State Commun. 27, 885 (1978).

[4]E. Zanazzi, F. Jona, D. W. Jepsen, and P. M. Marcus, Phys. Rev. B 14, 432 (1976).

[5]P. H. Citrin, P. Eisenberger, and R. C. Hewitt, Phys. Rev. Lett. 41, 309 (1978).

[6]No interfering edges or photoemission peaks from Cu lie within this range.

[7]P. H. Citrin, P. Eisenberger, and R. C. Hewitt, Phys. Rev. Lett. 45, 1948 (1980).

[8]P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid, Rev. Mod. Phys. 53, 769 (1981).

[9]P. H. Citrin, P. Eisenberger, and B. M. Kincaid, Phys. Rev. Lett. 36, 1346 (1976).

[10]A single second-nearest-neighbor Cu atom and four third-nearest-neighbor Cu atoms, all in the second layer, are calculated at 3.34 and 4.21 Å, respectively. The former gives zero signal for $\theta = 90°$ and is very weak for $\theta = 5°$, while the latter contributes a weaker signal for $\theta = 90°$ than for $\theta = 5°$ (the measured distances corresponding to position B in Fig. 1 in fact exhibit this latter small polarization dependence).

[11]O. K. Andersen, Phys. Rev. B 12, 3060 (1975); O. Jepsen, J. Madsen, and O. K. Andersen, Phys. Rev. B 18, 605 (1978).

[12]E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B 24, 864 (1981).

[13]A previous non-self-consistent calculation of the states at $\bar{\Gamma}$ could not distinguish between the mixed-layer and overlayer models; D. W. Bullett, Solid State Commun. 38, 969 (1981).

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

[15]D. Westphal and A. Goldmann, Solid State Commun. 35, 437 (1980); A. Goldmann and D. Westphal, Vacuum 31, 443 (1981). Note that these authors label the surface Brillouin-zone symmetry points according to the clean surface zone rather than the $c(2\times 2)$ zone as in this paper. Thus their $\bar{M}$ and $\bar{X}$ map into our $\bar{X}$ and $\bar{M}$ respectively.

[16]J. R. Smith, J. G. Gay, and R. J. Arlinghaus, Phys. Rev. B 21, 2201 (1980).

[17]M. J. Cardillo, G. E. Becker, D. R. Hamann, J. A. Serri, L. Whitman, and L. F. Mattheiss, unpublished.

[18]D. R. Hamann and L. F. Mattheiss, to be published.

[19]Photoemission lines from Ag interfere with Auger detection of the Cl *KLL* SEXAFS signal.