Oxygen-induced missing-row reconstruction of Cu(001) and Cu(001)-vicinal surfaces

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We have used x-ray-diffraction analysis to examine the structure of flat and vicinal Cu(001) surfaces under the influence of oxygen chemisorption. The initial electropolished vicinal surface consists of a fairly regular array of steps and terraces that preferentially orient the oxygen-induced reconstruction. Prolonged annealing leads to a hill-and-valley morphology with large (001) facets, upon which the preferential orientation is lost, just as for the flat surface. We find evidence for only one ordered phase as a function of oxygen coverage, which has $2\sqrt{2} \times \sqrt{2}$ symmetry. Crystallographic analysis of the diffraction data shows this to be a "missing-row" structure with 25% of the Cu sites vacant and large relaxations in the top layer. The oxygen site is not uniquely determined, however, with two distinct possibilities. This Cu(001)/O structure has a surprising similarity to that proposed for Cu(110)/O. In fact both surfaces can be decomposed into the same basic structural element, which is a Cu-O-Cu chain oriented along bulk [100] directions.

I. INTRODUCTION

Chemisorption on metals is usually discussed in terms of preferences between "adsorption sites," implying little or no modification to the substrate, and hence making little distinction from the structures expected with physisorption. The energies involved with the formation of covalent bonds, however, can easily exceed the energy per surface atom required to form kinks, steps, or other topological surface rearrangements associated with reconstruction. The kink energy is assumed to be of the order of the cohesive energy divided by the coordination. At the very least, adsorption can be expected to give rise to distortions in a substrate. Cases of adsorbate-induced reconstruction^{1,2} as well as adsorbate-induced facetting³ are known, but it is surprising they are not seen more often. The definition of the "equilibrium" state of a substrate-adsorbate system is not always clear because a sequence of locally stable or metastable states could exist. With oxygen on a metal as a function of time and/or temperature, for example, one might see first a pure adsorbate state without modification of the substrate, then induced reconstruction, followed by one or more oxide states and ending with bulk oxide formation. The exact preparation conditions must always be considered when comparing experimental results.

A good example of adsorbate-induced reconstruction is the Cu(001)/O system which was reported for many years to have both $\sqrt{2} \times \sqrt{2}$ (" $c2 \times 2$ ") and $2\sqrt{2} \times \sqrt{2}$ phases at different coverages based on qualitative low-energy electron diffraction (LEED) observations.⁴⁻⁸ None of the local structural studies so far has reported any clear difference between these states,⁵⁻⁷ and even LEED current-voltage (*I-V*) analysis of the half-order beams could not make the distinction.⁴ Models proposed were $\sqrt{2} \times \sqrt{2}$ adsorbates in the fourfold "hollow,"^{5,7} twofold "bridge,"^{4,8} or fivefold coplanar⁶ sites. The situation was recently clarified by Wuttig *et al.*⁹ who showed that, even dosing at room temperature, the $\frac{1}{4}$ order $2\sqrt{2} \times \sqrt{2}$) and $\frac{1}{2}$ order $(\sqrt{2} \times \sqrt{2})$ LEED spots appear *simultaneously* as a function of coverage and hence that there was no ordered $\sqrt{2} \times \sqrt{2}$ phase at all. The $\frac{1}{4}$ order reflections are much weaker and simply may not have been seen at low coverage above the background of a typical displaytype LEED apparatus.

Wuttig et al.⁹ also argued by symmetry analysis of electron energy-loss spectra (EELS) that the Cu(001) substrate was also reconstructed. Since then there was a LEED *I-V* study¹⁰ of the $2\sqrt{2} \times \sqrt{2}$ structure suggesting a "missing-row" class of model, a very dramatic form of reconstruction in which one out of four rows of surface Cu sites is vacant. Our x-ray diffraction analysis arrives immediately at the same conclusion. We will then show by least-squares refinement of the atomic coordinates that there is considerable distortion of the basic structure and obtain an indication of the oxygen binding site.

The $2\sqrt{2} \times \sqrt{2}$ reconstruction has lower symmetry than the clean unreconstructed Cu(001) substrate. This leads to a "twinning" of the surface into two domains that are presumed to be randomly distributed on the flat surface. Stepped surfaces, however, have present a symmetry-breaking force which can polarize the domain distribution, as has been seen on the W(110)/H (Ref. 11) and Si(100) (Ref. 13) reconstructed surfaces. This is somewhat analogous to the polarization of surface domains in an external mechanical strain field.¹³ We have employed the polarization effect to avoid the crystallographic degeneracy that arises from twinning to facilitate our structure determination.

Diffraction from stepped surfaces is an interesting sub-

ject in its own right¹⁴ and allows information about the distribution of steps to be obtained. The general morphology of a surface changes with preparation conditions and will in time reach an equilibrium state that is either a regular staircase of steps and uniform terraces (i.e., "flat"), or else decompose into facets of lower crystallographic index ("hill-and-valley" structure). The "Wulff construction"¹⁵ theory of equilibrium crystal shapes allows predictions to be made, based on the orientation dependence of the surface free energy. Since this energy changes with temperature, phase transitions in the equilibrium crystal shape are expected and are indeed observed.¹⁶ It is also expected that the presence of a reconstruction on one or more of the crystallographic faces will significantly modify the energy balance between flat (regular staircase) and facetted (hill-and-valley) configurations, as has been seen in studies of vicinal Si(111) surfaces.¹⁷

II. EXPERIMENTAL DETAILS

The measurements were made at beamline X16A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, a station dedicated to surface x-ray diffraction. Five milliradians of bending magnet radiation were monochromated to a wavelength of about 1.5 Å by Si(111) crystals. This beam was focused onto the sample held inside an ultrahigh vacuum diffractometer¹⁸ at a pressure of 3.5×10^{-10} Torr. Angular settings for in-plane and out-of-plane diffraction were calculated in the five circle mode.¹⁹ The alignment made use of two bulk Bragg peaks as reference points. Measurements were made in a "surface" reciprocal coordinate frame (as used in LEED) defined by means of a transformation from the bulk frame:

h		$\frac{1}{2}$	$\frac{1}{2}$	0	h		
k	=	$\frac{1}{2}$	$-\frac{1}{2}$	0	k		
$\left[l \right]$	surface	0	0	1	[1]	bulk	

The detector was a NaI scintillator behind $2 \times 10 \text{ mm}^2$ slits 0.5 m from the sample when radiation of 8 keV was used. To reach a larger range of momentum transfer, 11 keV radiation was also employed along with an intrinsic Ge detector to remove Cu fluorescence.

Two different samples were studied. Sample A was a 12 mm diameter disk cut from a Cu crystal within 0.5° of (001); sample B was a similar size but cut about 2° away from (001) along a direction within 10° of the $[1\bar{1}0]_{surface}$ azimuth. Each sample was mechanically polished and then electropolished in 70% H₃PO₄ at 2.0 V and 0.2 A cm⁻² for several minutes. An optical mirror surface was not obtained by this procedure as some pitting took place. At the end of polishing the samples were bright and shiny instead of dull. Once inside the vacuum they were cleaned by cycles of sputtering and annealing at 500°C. Sulfur segregation ended after 2 days of treatment and no other contaminant was seen. Oxygen dosing was usually carried out at 300°C and 10⁻⁶ Torr. Doses up to 1000 L [1 L (langmuir)=10⁻⁶ Torrs] of O₂, followed by annealing at 400°C produced sharp $\frac{1}{2}$ order and

 $\frac{1}{4}$ order x-ray diffraction peaks. We investigated much lower doses of O₂ to look for evidence of a $\sqrt{2} \times \sqrt{2}$ phase, but found that both $\frac{1}{2}$ order and $\frac{1}{4}$ order x-ray peaks appeared simultaneously, in agreement with the findings of Wuttig *et al.*⁹

Diffraction line shapes were measured by index scans in the $(h,k,l)_{\text{surface}}$ reciprocal lattice, usually scanning in the $[1\overline{10}]_{\text{surface}}$ and $[110]_{\text{surface}}$ directions, perpendicular and parallel to the steps of sample *B*. The instrumental resolution, set by the slits, was, therefore, in some oblique direction. Most of the features seen were broader than resolution, so this was not important to the results.

Crystallographic data were obtained by numerical integration of ϕ scans centered around the $(h,k,l)_{surface}$ point of interest. Integrated intensities were corrected for the Lorentz factor and active sample area.²⁰ These included out-of-plane measurements up to $q_1 = 1.0$ Å $^{-1}$, obtained by the setting of the fifth axis (called the α axis) underneath the standard four-circle diffractometer such that the surface normal was approximately horizontal.¹⁹ The incident and exit angles were always kept larger than 2° in order that the intensities were neither enhanced by total external reflection nor eclipsed by shadowing of the etch pits in the surface. The data were averaged over symmetry equivalents to obtain an agreement factor, R, for strong reflections only. This is taken to be a measure of systematic error²⁰ and was subsequently used to apply statistically correct weighting to the data in the leastsquares refinement. Refinement was carried out with the PERSONAL SDP crystallography programs.²¹

The 260 fractional-order reflections of sample A yielded a dataset of 4 $\frac{1}{2}$ orders and 15 $\frac{1}{4}$ orders with R = 0.17. This relatively large agreement factor may be related to sample miscut (see below) although this was not detectable at the time. Sample B produced several datasets with different preparation conditions, the best of which started with 80 reflections and yielded 4 $\frac{1}{2}$ orders and 16 $\frac{1}{4}$ orders with R = 0.05.

III. SURFACE MORPHOLOGY

Once clean, with or without oxygen, sample A only gave diffraction intensity along rods parallel to the crystallographic [001] direction. Its surface therefore comprised crystallographic (001) facets of a size given by a coherence length, $L = a_1 / \pi \Delta h_{\text{FWHM}}$, where a_1 is the surface lattice parameter (2.556 Å), of order 100 Å. FWHM denotes full width at half maximum. This was not limited by instrumental resolution. The miscut sample B, on the other hand, showed time-dependent behavior as shown in Fig. 1. The first curve shows a $[1\overline{10}]$ scan across one of the fractional-order peaks of the Cu(001)/O $2\sqrt{2}\times\sqrt{2}$ reconstruction measured near $(0.75, -0.75, 0.4)_{surface}$ and taken soon after the sample was prepared initially. The broad peak, shifted away from the exact quarter position signifies that the surface is stepped.¹⁴ Similar behavior was found for the integerorder rods (also present on the clean 1×1 surface) that arise from crystal truncation²² [crystal truncation rod (CTR)]. A sharp, shifted integer-order peak (perhaps



FIG. 1. Evolution of the line shape of the Cu(001)/O reconstruction as a function of time. These are scans of the $(0.75, -0.75, 0.4)_{surface}$ peak taken along the $[1\overline{10}]_{surface}$ direction, perpendicular to the steps. The elapsed time marked is only an approximate indication of the number of cycles of cleaning which was found to change the surface morphology, but was not quantified carefully. The horizontal axis is calibrated in reciprocal lattice units (r.l.u.) of the surface Cu coordinate frame defined in the text.

with satellites) would indicate a perfect, regular staircase of equal-sized terraces;¹⁴ the broad peak we see implies some distribution of sizes. Over the course of two weeks of sputtering, annealing and oxygen dosage, this distribution evolved as shown, passing through a state with two clear peaks, and ending up with a sharp peak at the crystallographic $(0.75, -0.75, 0.4)_{surface}$ position and a long asymmetric tail on the [110] side. The surface is undergoing phase separation into large (100 Å) regions of [001] orientation and regions with high densities of steps whose orientation is not determined. The total number of steps is, of course, constrained by the gross miscut angle of 2°, corresponding to one step every 50 Å on average.

The equilibrium state is presumably the exact [001] direction for both samples A and B, but for the latter it takes much longer for the facet to grow flat because this involves the slow redistribution of a greater number of atoms. This statement is, of course, applicable only to the particular preparation recipe we used, because that affects the equilibrium. We did not see any evidence of reversibility of the trend towards the facetted state. Very different behavior was seen for miscut Cu(110) where rapid reversible switching was seen between a facetted clean surface and a regularly stepped oxygen-covered one.³ We did not explore sufficiently wide variations of surface preparation conditions to determine whether or not the initial regular- stepped state of sample B could be regenerated in vacuum, although we assume that another cycle of electropolishing would achieve this.

Figure 2 shows the line shape of the $(0.75, -0.75, l)_{surface}$ reflection measured at early time (i.e., on a staircase substrate) by scanning along [110],



FIG. 2. Scans of $(0.75, -0.75, l)_{surface}$ peaks taken at early time along the $[1\overline{10}]_{surface}$ direction at different values of perpendicular momentum transfer l=0.1, 0.2, 0.3, and 0.4. Each vertical scale is normalized to unity. The locus of the peak positions is a straight line passing through the exact quarter-order position. The top curve is the same as shown in Fig. 1. The horizontal axis is calibrated in reciprocal lattice units (r.l.u.) of the surface Cu coordinate frame defined in the text.

displayed at different heights along the rod, i.e., as a function of the perpendicular momentum transfer, l. Several interesting conclusions can be drawn. First, the $\frac{1}{4}$ order rod is tilted with respect to the crystallographic direction. This means that the reconstruction is coherent across steps, with a fixed phase relation between adjacent terraces. The average angle of inclination is 3°, about the same as the miscut angle. Second, the peak is narrow in plane (near l=0) and broad out of plane. This rod widens with perpendicular momentum transfer in a similar way to the integer-order CTR. This implies that the lateral phase shift of the reconstruction upon crossing a step is zero: the reconstructed domains on adjacent terraces are not only coherent but in phase. The consequences of this will be discussed further in Sec. V after we have deduced an atomic model of the surface.

A further effect of this close association between the steps and the reconstruction is that there is strong polarization of the domains, as illustrated in Figs. 3 and 4. Figure 3 is a schematic diffraction pattern showing that the $\frac{1}{4}$ orders of the two domains appear in different reciprocal space positions, while the $\frac{1}{2}$ orders coincide. Our convention is that the (0.75, -0.75, l) rod comes from "domain 1" while the (0.75, 0.75, l) rod comes from "domain 2." This convention is illustrated in real space as Fig. 3(b) which shows the step and the unit-cell orientations for both domains. Figure 4 compares the $\frac{1}{4}$ order

step direction $[1\overline{10}]$. At early time when the substrate is a staircase of narrow terraces, there is about 90% polarization: the domain 2 peak is very small indeed. Interestingly, this peak is narrow and centered, as if arising from a large (001) facet. As the substrate evolves towards the large facet state at long times, the domain ratio equalizes and the peaks begin to look the same. At intermedi-

izes and the peaks begin to look the same. At intermediate times, a two peak line shape is seen for domain 1, with one sharp peak centered at the crystallographic position and a broad shifted one to the side. The domain 2 peak always has the same shape.

Clearly domain 1 is the orientation favored by the steps: the fixed phase shift implies a structural interaction between the step and the domain 1 reconstruction, and the staircase state of the surface (early time) is practically all domain 1. Domain 2 appears only when large (001) facets have finally formed, and most of the steps have



FIG. 3. (a) Plan view of the diffraction pattern of the Cu(001)/O $2\sqrt{2} \times \sqrt{2}$ structure in the $(h,k,l)_{surface}$ coordinate frame showing the superposition of the two rectangular domains. The integer-order reflections ("1×1" LEED spots) are marked two ways to indicate the centering of the fcc lattice. Those denoted crystal truncation rods (CTRs) are positions for which the bulk Bragg peak is out of plane (i.e., at *odd* values of l), while the others are in-plane bulk. (b) Real-space picture of the Cu(001) substrate with the same orientation as (a). The unit cell of the oxygen-induced reconstruction is drawn for the two different domains. Some steps are drawn with the orientation found on sample B; their proximity is exaggerated. Unit-cell boxes for the two domain orientations of the $2\sqrt{2} \times \sqrt{2}$ reconstruction are defined.



FIG. 4. Diagram showing the shifts of symmetry equivalent quarter-order reflections (a) at early time just after cleaning the electropolished surface and (b) a week later after many cycles of cleaning. Scans are taken along the $[1\overline{10}]_{surface}$ direction. The domain 1 peak at $(1.75, 0.25, 0.3)_{surface}$ and the domain 2 peak at $(1.75, -0.25, 0.3)_{surface}$ are different at early time but become truly equivalent later. The horizontal axis is calibrated in reciprocal lattice units (r.l.u.) of the surface Cu coordinate frame defined in the text.

coalesced far away. At that time, both domains are more or less randomly distributed on the facets and so their diffraction peaks appear similar. Diffraction from the phase separated, heavily stepped regions left over is presumably very diffuse and so barely detected, as with the clean surface.

IV. MISSING-ROW MODEL

The atomic arrangement of the reconstruction can be obtained by a crystallographic analysis of structure factors, which are the square roots of integrated intensity values. This is not a problem for $\frac{1}{4}$ order reflections that appear separated in reciprocal space, as Fig. 3 shows. However, at the $\frac{1}{2}$ order positions, two nonequivalent reflections are superimposed. In order to estimate the separate contributions here, we took advantage of the asymmetry of twinning caused by the steps on sample B. Surveying the four equivalent positions of $(\frac{1}{2}, \frac{1}{2}, 0.3)$ and eight equivalent positions of $(1\frac{1}{2}, \frac{1}{2}, 0.3)$ on this sample at early time, we found a clear pattern. Figure 5 shows the first of these acts. Half of the peaks are broad and shifted, reminiscent of the $\frac{1}{4}$ orders of domain 1, while the others are small, narrow, and centered, as for domain 2. Since no split peak was seen, as would be expected for the superposition of both domains, we are forced to conclude that the $(\frac{1}{2}, -\frac{1}{2}, l)$ structure factor of domain 1 is large while the $(\frac{1}{2}, \frac{1}{2}, l)$ value is undetectably small; the converse would be true of the rotated domain 2, if it were present at early time. The same story applies to the other reflection: $(1\frac{1}{2}, \frac{1}{2}, l)$ is small and $(1\frac{1}{2}, -\frac{1}{2}, l)$ large for domain 1 and the reverse for domain 2. Knowing this, we can safely assign the observed $\frac{1}{2}$ order intensity in



FIG. 5. Diagram showing the shifts of symmetry equivalent half-order reflections at early time. Scans are taken along the $[1\overline{10}]_{surface}$ direction as shown in the inset. The pattern is very similar to that of the quarter-orders with two narrow centered peaks and two large shifted ones, in spite of the fact that *both* domains are superimposed. The horizontal axis is calibrated in reciprocal lattice units (r.l.u.) of the surface Cu coordinate frame defined in the text.

each crystallographic dataset to the appropriate reflection, and set the other of the pair to a low value.

For sample A, an extensive set of measurements was made as a function of perpendicular momentum transfer, l, but these showed almost no change from the in-plane values. This indicates immediately a single-layer structure, so subsequent analysis was carried out in two dimensions. Symmetry equivalent measurements, including the various l points, were averaged together to yield a two-dimensional (2D) dataset. Separate datasets were collected for the two domains of sample B. Because of the peak broadening in l (Fig. 2) and the miscut, the data on domain 1 at early time had peaks that were not properly integrated and were not usable (R > 0.20); the latertime data on domain 1 were properly centered and usable. The dataset with the best internal agreement was for domain 2 of sample B at later time (R = 0.05). The crystallographic results presented refer to this best dataset, but all details except the overall scale factor were totally consistent for all three sets of data.

Without prior assumptions about the structure, we started by analyzing the data by the usual means of a Patterson function,²⁰ shown in Fig. 6(a). We expect to locate the Cu atoms first because oxygen atoms would scatter much more weakly. Since the expected structure is strictly two dimensional, we look first at the peaks beyond a radius from the origin equal to the Cu—Cu bond length. The Patterson is somewhat reminiscent of that of Au(110),²³ with a strong diagonal nonorigin peak, indicating a 2D structure with three atoms per unit cell as before.²³ This model is drawn in Fig. 6(b), the two large radius interatomic vectors corresponding to Patter-

son peaks as shown. The third (small radius) peak in the Patterson is related to oxygen and is discussed in Sec. IV.

Least-squares refinement of the model in Fig. 6(b) gave a reasonable fit to the data with $\chi^2 = 11$. Most of the disagreement lay with the $\frac{1}{2}$ orders, which the model predicts in the order *reversed* from that seen in Fig. 5; the $\frac{1}{4}$ orders alone gave $\chi^2 = 3.5$.

The atom marked Cu(1) has no degrees of freedom. Atom Cu(2) is displaced along the [11]_{surface} axis²⁴ from the nearby bulk site by 0.33 ± 0.04 Å. The third atom in the $2\sqrt{2} \times \sqrt{2}$ unit cell [dashed line in Fig. 6(b)] that would make up a complete layer of Cu is missing. Thus the basic structure of Cu(001)/O $2\sqrt{2} \times \sqrt{2}$ is of the missing-row type. Unlike Au(110) 1×2 (Ref. 23) it is not a close-packed row of atoms that is missing, but one out of four open [100]_{bulk} rows. The Cu "coverage" in the top layer is therefore 0.75. The atoms of this layer are then spread out partially to fill the gap that is left behind.

V. OXYGEN SITE

Presumably the remaining discrepancy in the fit to the model above is due to the oxygen atoms, which were located next. The scattering power of oxygen is considerably smaller than that of Cu by virtue of having fewer electrons, so the oxygen can be regarded as a perturbation of the basic Cu structure. As noted above, the 3 Cu arrangement alone, while fitting the $\frac{1}{4}$ orders fairly well, totally miscalculated the intensity of the $\frac{1}{2}$ orders. This effect can be understood to be due to the superposition of



FIG. 6. (a) Contour map of the 2D Patterson function inside the full $2\sqrt{2} \times \sqrt{2}$ unit cell with *Pmm2* symmetry. The orientation is defined in Fig. 3(b). Positive contour levels only are shown with the first level removed for clarity. (b) Interpretation of the Patterson with a three-atom model. Vectors A and B reproduce the peaks of the map. Dashed atoms are the positions in a bulk layer.

an approximately $\sqrt{2} \times \sqrt{2}$ arrangement of oxygen atoms, that would contribute to the $\frac{1}{2}$ orders but not the $\frac{1}{4}$ orders, thereby allowing a good fit to the latter with only the Cu part of the structure. Testing the four possible ways of superposing a $\sqrt{2} \times \sqrt{2}$ array of oxygen atoms favored the site between two adjacent Cu bordering the missing row.

Supporting evidence for this site comes also from further interpretation of the Patterson function in Fig. 6. The third peak is too close to the origin to correspond to a flat Cu—Cu bond, but is appropriate for Cu—O. Because there is more than one Cu in the unit cell, this does not uniquely specify the site, but limits the choice to bridging sites parallel to the missing row.

The site is most dramatically indicated in the difference map of Fig. 7, obtained by summing the Fourier series of $(F_{observed} F_{calculated})$ coefficients using phases calculated from the 3 Cu structure.²⁰ Since this site lies on a mirror line, it has one degree of freedom in the plane. Although addition of the extra atom led to a much better fit, leastsquares refinement of the oxygen position was not very effective, maybe because the oxygen contributes so weakly to the structure. Closer investigation revealed a *double minimum* in χ^2 , caused by a strong negative correlation between the Cu and O atomic displacements. This was



present for all three datasets and, moreover, could not be removed by use of out-of-plane data, since both structures are essentially 2D. The two solutions are drawn in Figs. 7(b) and 7(c) and their agreement with the observed data is shown in Fig. 8. It is clear that the diffraction patterns are very similar indeed and that we cannot distinguish between them.

We thus obtained the two final 2D models after refinement of two positional coordinates, $y_{Cu(2)}$ and y_0 , given as fractions of the long axis lattice constant, 7.23 Å. The refined values were $y_{Cu(2)}=0.284(2)$ and



FIG. 7. (a) Positive contours of a Fourier map of the differences between observed structure factors $(\frac{1}{4} \text{ and } \frac{1}{2} \text{ order})$ and those calculated from the 3 Cu atom model (positions indicated). Phase are taken from that model. A clear peak shows the location of the oxygen atom in the unit cell. (b) and (c) Final refined models of the lower half of the $2\sqrt{2} \times \sqrt{2}$ unit cell showing the two solutions I and II.

FIG. 8. Histogram comparing observed and calculated structure factors for final models I and II in Fig. 7. The indexing convention is for domain 2 (Fig. 3). The top panel shows the $\frac{1}{2}$ orders, while the lower panels show the $\frac{1}{4}$ orders laid out in diagonal rows (Fig. 3). The alternation of weak and strong reflections is characteristic of the displacements in the missingrow atomic arrangement (Ref. 22).

 $y_0 = 0.320(9)$ for model I in Fig. 7(b) giving $\chi^2 = 3.84$ and $y_{Cu(2)} = 0.293(3)$ and $y_0 = 0.280(10)$ for model II in Fig. 7(c) with $\chi^2 = 4.28$. The lateral Cu displacements from their corresponding bulk sites were 0.25 ± 0.02 Å and 0.31±0.02 Å, respectively. Thermal Debye-Waller parameters were fixed at the bulk value²⁵ of 0.5 Å²; refinement of these was not found to lead to any improvement in χ^2 or to any significant deviations. The agreement of both models is shown diagrammatically in Fig. 8. The biggest disagreement is for the $(1\frac{1}{2}, -\frac{1}{2})_{surface}$ reflection, which completely dominates χ^2 . This is attributed to a slight error in the relative normalization of $\frac{1}{2}$ order and $\frac{1}{4}$ order data that arises from incomplete integration of the intensities; the $\frac{1}{2}$ orders were always slightly narrower than the $\frac{1}{4}$ orders for reasons not determined. With this caveat we believe the fit of both models to be satisfactory, given the present accuracy of the data.

The important question of bond lengths is clouded by the uncertainty of the oxygen position: the double solution means we cannot even determine the coordination, as Fig. 7 shows. The Cu(1)-O distance [projected onto the (001) plane] is either 2.02(7) Å, a value consistent with the average bond length in bulk CuO (tenorite) of 1.96 Å, 26 or else 2.31(7) Å indicating no bond at all. The Cu(2)-O projected distance is 1.81(1) Å or 1.83(1) Å, a little shorter than 1.84 Å in Cu₂O (cuprite),²⁶ but this number would be larger if there were a sufficient difference in the heights of the atoms. There is also the possibility of one more Cu-O bond to the layer below. The coordination of the oxygen in model II is 4 with a distorted tetrahedral arrangement, as in both cuprite and tenorite. The coordination in model I is 3 or possibly even 2 depending on the interlayer distance.

It is expected, in general, that any nonprimitive structure must contain a certain degree of 3D character, either in the form of second-layer displacements or buckling of a mixed layer of atoms.²⁷ We calculate an upper limit of 0.5 Å for the relative perpendicular component of the Cu positions, based on keeping the q_{\perp} dependence of various reflections constant within their error bars. The large lateral displacements of the Cu atoms would certainly imply a certain amount of out-of-plane motion as well (to avoid close contacts with the layer below) but this is still less than 0.5 Å.

VI. COMPARISON WITH PREVIOUS WORK

Next we consider the earlier experimental data on Cu(001)/O and the extent to which they are consistent with our model. The extended x-ray-absorption finestructure (EXAFS) measurements,⁷ even though they led to the incorrect conclusion of the fourfold hollow site, were based on experimental determinations of a bond length of 1.94(4) Å and a polarization amplitude ratio $A(90^{\circ})/A(45^{\circ})$ of 1.4 ± 0.2 . The bond length is consistent with the tetrahedral fourfold site of model II, considering that the data cannot separate a spread of bond lengths less than ~0.1 Å, and the large uncertainty in our vertical distance determination. The 2.3 Å Cu-O distance of model I should be distinguishable by EXAFS, but the Fourier transform of the measured spectrum⁷ is too noisy to decide. Model I gives $A(90^\circ)/A(45^\circ)=1.0$ while model II gives $A(90^\circ)/A(45^\circ)=1.2$ because one more in-plane bond contributes. Thus EXAFS seems to favor model II with the fourfold tetrahedral site. A further complication is that distinctly different EXAFS data are obtained at lower coverages of O on Cu(001), perhaps corresponding to a disordered site;²⁸ it is therefore not clear that the published data,⁷ taken after 300 L exposure, came from a pure $2\sqrt{2} \times \sqrt{2}$ structure.²⁹

The most careful measurement of oxygen coverage in the $2\sqrt{2} \times \sqrt{2}$ structure⁹ gave $\Theta_0 = 0.48 \pm 0.05$ in good agreement with the model. The pattern of streaking of $\frac{1}{2}$ order LEED spots along [110]_{surface} and [110]_{surface} directions⁸ was previously interpreted as indicating twofold bridge oxygen sites. We saw streaking in one of these directions due to steps, but it would also be expected on a flat surface because of an anisotropic domain shape with better order along the missing-row direction than across it. Therefore we believe the missing-row model to be completely consistent with this observation. We are not able to comment on the consistency of the model with normal photoelectron diffraction^{5,6} or EELS (Ref. 9) results because these require involved subjective calculations. The LEED I-V (Ref. 10) analysis found reasonable agreement with missing-row models and preferred the same oxygen site, but without any distinction between models I and II. Very recently two new studies have emerged, both confirming the missing-row structure: one is a parallel combination of LEED and scanning tunneling microscopy;³⁰ the other is a combination of x-ray absorption and photoelectron diffraction.³¹

VII. NATURE OF RECONSTRUCTED STEPS

The knowledge of an atomic model for the $2\sqrt{2} \times \sqrt{2}$ unit cell and the fact that the reconstruction is coherent (in projection) across the steps, as shown in Sec. III and Fig. 2, leads us to propose a structure for the steps. This is drawn in Fig. 9 as a plan view and Fig. 10 in cross section. We also derive schematically in Fig. 10 the diffraction pattern seen in Fig. 2.

The missing-row structure can be considered to be made up of two $[1\overline{10}]_{surface}$ (i.e., $[100]_{bulk}$ oriented steps facing each other. We can therefore propose that the step at the end of each terrace of sample *B* has the same reconstruction as in the $2\sqrt{2} \times \sqrt{2}$ unit cell, with an O-Cu-O chain as shown. In order to build in a specific phase relation between the adjoining terraces, we must continue immediately with a missing row in the terrace below. This arrangement is rationalized below, but first we will show how this predicts the broadening and shifting of the $\frac{1}{4}$ order diffraction we saw in Fig. 2.

The important consequence of this fixed phase relationship is that the terraces must be an integer multiple of reconstructed unit cells wide, although there can be disorder in the exact number of unit cells involved. Further experimental evidence in favor of this situation is that (1,0,4) is a favored facet direction in the presence of oxygen.³² Figure 10 shows three ideal *regular* staircase structures, of, respectively, (1,0,8), (1,0,12), and (1,0,16)orientation, which are natural extensions of the known



FIG. 9. Scale drawing of the top view of a Cu(001)/O surface containing steps perpendicular to $[1\overline{10}]_{surface}$ (arrows). Solid circles are oxygen; open circles are Cu. Boxes denoting the $2\sqrt{2} \times \sqrt{2}$ unit cell (domain 1) are added to emphasize the polarization of domains by the steps.



FIG. 10. (a)–(c) Side view of regular step arrays abstracted from the Cu(001)/O reconstruction. Open and solid circles represent atoms in the plane of the page and in the plane behind, as required by the fcc lattice centering. Diffraction patterns consisting of arrays of δ -function rods are derived by Fourier transformation of the array of step edges (Ref. 14). The dots represent bulk Bragg peaks. The "upper level" of the pattern that passes through the bulk (101)_{surface} peak, is shifted by half a rod spacing because of the lattice centering, but is omitted for clarity. (d) Superposition of these diffraction patterns. (e) Closeup of the region of interest near (0.25, -0.25,0)_{surface}.

(1,0,4) facet direction.³² The diffraction patterns are then derived using standard arguments.¹⁴ When these are superimposed in Fig. 10(d), we find that rods from all abstractions pass exactly through the points $(\frac{1}{4}, -\frac{1}{4}, 0)_{surface}$, $(\frac{1}{2}, -\frac{1}{2}, 0)_{surface}$, etc., but spread out in a fan out of plane. Disorder in the terrace widths, corresponding to an *irregular* staircase, will have the effect of smearing the fan into a distribution similar to that seen in Fig. 2.

Finally, we examine the structural model for Cu(001)/O and compare it with the behavior of oxygen on other faces of Cu. First we consider Cu(110)/O, which is also believed to have a missing-row-type structure,² although of a rather different kind. For an ordered structure, this is of course identical to an "added row" configuration.³³ Figure 11 compares side views of these structures and reveals a few interesting similarities between them. We have chosen vertical coordinates for the purpose of illustration to give the same local configuration for both (110) and (001) surfaces and forced the oxygen in the Cu(110)/O structure to be in a site of full 2mm symmetry. The row of atoms missing in each case has the same [100]_{bulk} direction and the oxygen inserts into the open row left behind in both cases, which is the "long bridge" site of Cu(110). Because we have two possibilities for the in-plane Cu(001)/O structure, we show two versions (a) and (b) of Fig. 11. The lateral uncertainty in the exact position of the oxygen in Cu(001)/O, if all these assumptions of similarity are correct, manifests itself in a vertical uncertainty in Cu(110)/O: the oxygen could be either just below or just above the top Cu(110) layer. Ironically, the experimental situation for Cu(110)/O (Refs. 2, 33, and 34) is also un-



FIG. 11. Scale drawing of the Cu(001)/O, Cu(110)/O, and Cu(104)/O reconstructions viewed from the side, looking along the missing rows. Solid circles are oxygen; open circles are Cu. The same local geometry can be inferred for all surfaces, with the same juxtaposition of missing rows and O-Cu-O chains. The steps of the Cu(104)/O structure can be considered to be a reconstructed (110) microfacet with (001) terraces on each side. Panels (a) and (b) refer to solutions I and II of the local structure, but this does not affect the general situation. Some license has been taken with the vertical coordinates of Cu(001)/O, which are not known: they have been chosen to retain mirror symmetry in the Cu(110)/O structure in each case.

certain on this point, although the subsurface site is slightly favored.²

Secondly, Fig. 11 shows a proposed structure of the Cu(104)/O surface, assuming an analogous oxygeninduced reconstruction mechanism. This structure naturally explains the stability of the (104) face over other vicinals in the presence of adsorbed oxygen.³² It is the staircase structure with the densest packing of the steps used in Fig. 10. The proposed step structure has the unusual feature of a double height rise where a missing row immediately follows the step edge: this is readily understood, however, because this arrangement is also a component of the Cu(110)/O reconstruction.

Following this reasoning, it is interesting to conclude that the Cu(001) surface is forming stable Cu(110)/O microfacets when it reconstructs. This is just the reverse of the situation for many clean metal (110) surfaces which reconstruct to expose close-packed facets of *lower* index.³⁵ A different kind of driving force seems to be involved. Clean metal surfaces try to maximize surface coordination, whereas these oxygen-covered surfaces

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adopt structures that are stabilized by Cu-O-Cu-O-Cu chains directed along $[100]_{bulk}$. The Cu atoms in these chains have a relatively low coordination number, and are presumably covalently bonded. Chains are now seen in five separate structures: Cu(001)/O, Cu(110)/O, Cu(104)/O, the steps on vicinal Cu(001)/O, and also as isolated chains in low coverage Cu(110)/O surfaces studied by scanning tunneling microscopy.^{33,34} Not only is the choice of $2\sqrt{2} \times \sqrt{2}$ reconstruction of Cu(001)/O itself explained by the chain hypothesis, but also its strong orientational preference of the domain with the chain parallel to the step edge (domain 1) in staircase (early-time) stepped surfaces.

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FIG. 6. (a) Contour map of the 2D Patterson function inside the full $2\sqrt{2} \times \sqrt{2}$ unit cell with *Pmm2* symmetry. The orientation is defined in Fig. 3(b). Positive contour levels only are shown with the first level removed for clarity. (b) Interpretation of the Patterson with a three-atom model. Vectors *A* and *B* reproduce the peaks of the map. Dashed atoms are the positions in a bulk layer.



FIG. 7. (a) Positive contours of a Fourier map of the differences between observed structure factors $(\frac{1}{4} \text{ and } \frac{1}{2} \text{ order})$ and those calculated from the 3 Cu atom model (positions indicated). Phase are taken from that model. A clear peak shows the location of the oxygen atom in the unit cell. (b) and (c) Final refined models of the lower half of the $2\sqrt{2} \times \sqrt{2}$ unit cell showing the two solutions I and II.