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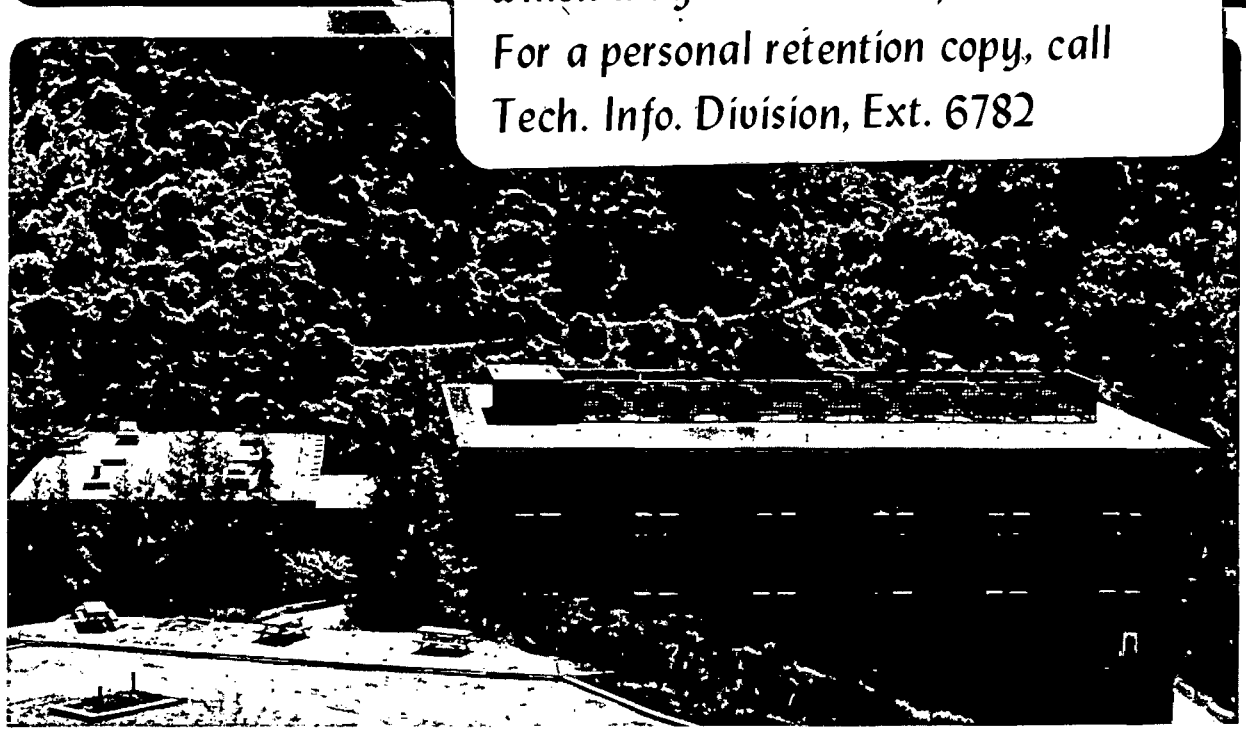

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NORMAL PHOTOELECTRON DIFFRACTION OF O/Cu(001): A SURFACE STRUCTURAL DETERMINATION

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ABSTRACT

The two systems c(2x2)O/Cu(001) and ($\sqrt{2}$ x $2\sqrt{2}$)R 45° O/Cu(001) have been studied by normal photoelectron diffraction (NPD), using the O(1s) line. In the c(2x2) structure, oxygen occupies the fourfold hollow site, with $d_\perp$ = 0.80(5) Å. The $\sqrt{2}$ x $2\sqrt{2}$ structure has a similar NPD curve, indicating the same local site geometry for the c(2x2) sublattice.

Oxygen adsorbs on Cu(001) with difficulty, producing a c(2x2) structure at low exposures and a ($\sqrt{2}$ x $2\sqrt{2}$) R45° structure at higher exposures (Figure 1B). Recent studies of the c(2x2) structure by azimuthal photoelectron diffraction,[1] angle-resolved SIMS,[2] and low energy ion scattering plus low energy electron diffraction (LEED),[3] have yielded conflicting results: hollow site ($d_\perp$ = 0.0(1) Å), hollow structure ($d_\perp$ = 1.2-1.5 Å), and bridge structure ($d_\perp$ = 1.4 Å), respectively. In this Communication we report oxygen (1s) NPD studies[4] on both structures that rule out all the above geometries for the c(2x2) structure.

Two of the above experiments[1,2] did not employ in situ LEED analysis, which creates ambiguities because of the propensity of the c(2x2) structure to develop additional ($\sqrt{2}$ x $2\sqrt{2}$) R45° spots. In our experiments, extremely weak ($\sqrt{2}$ x $2\sqrt{2}$) R45° spots were observed after the completion of NPD data collection on each of our c(2x2)O/Cu(001) samples, 30-70 hours after sample preparation. This sample evolution was contrary to our experience with all other samples studied with NPD.[4] This led us to perform NPD measurements on deliberately prepared ($\sqrt{2}$ x $2\sqrt{2}$) R45° O/Cu(001) samples. Beam dosing exposures of 400 Langmuirs were used to obtain the c(2x2) structure and 4000 Langmuirs for the ($\sqrt{2}$ x $2\sqrt{2}$) R45° structure, each being followed by annealing to 375 K for four minutes.

These experiments were performed at the Stanford Synchrotron Radiation Laboratory on Beam Line I-1 using an apparatus described elsewhere.[5] Auger spectroscopy, photoemission, and LEED were used to check surface cleanliness and ordering. Any S and O impurities were

below detectable levels and C/Cu Auger intensity ratios were less than 0.005. The purity of the oxygen exposures was monitored by a residual gas analyzer. Excellent internal agreement was obtained among two NPD curves from two c(2x2) samples and three NPD curves on two $\sqrt{2}$ x $2\sqrt{2}$ samples.

The three NPD curves in Fig. 1A show normalized O(1s) peak intensities plotted against kinetic energy. Curves a and b represent the same data for c(2x2)O/Cu(001), normalized to photon intensities in two different ways. In the conventional external method (curve a), the relative photon intensity is determined by a gold grid-channeltron assembly.[4] A preferred new internal method (curve b) was developed that employs the background electron intensity at a kinetic energy above the O(1s) peak, normalized to secondary electron cross sections.[6] The latter method is preferred because the photon intensity and cross section measurements are made simultaneously by the same detector observing a single section of the photon beam. The two curves show very good agreement. Curve c, for the sample ($\sqrt{2}$ x $2\sqrt{2}$) R45° O/Cu(001), is based on the internal method.

The c(2x2) curves were compared with scattering theory [7,8] in three ways. The first and most orthodox comparison with theory consists of matching theoretical and experimental curves, with special attention to peak positions. This was done exhaustively, using theory curves computed for a wide range of possible structures, including the coplanar hollow geometry. Particular emphasis was placed upon the results of the previous experiments. [1-3] With the exception of the hollow site ,

$d_\perp$ = 0.8 Å case, no other structure gave an NPD curve in even remotely acceptable agreement with experiment. The curve for the adopted structure shows excellent agreement for every peak position, even at the highest and lowest energies (Fig. 2a,b), with the exception of the features near 80eV. A detailed comparison of experimental peak positions with theoretical curves was made at closely spaced $d_\perp$ intervals around 0.8Å. This yielded consistent results for all features, with the conclusion that $d_\perp$ = 0.80(5)Å. This corresponds to a Cu-O distance of 1.97(3)Å, in close agreement with the bond length of 1.95Å in CuO. This result is similar to those for c(2x2)O/Ni(001): $d_\perp$ = 0.85(4)Å [9] and $d_\perp$ = 0.86(7)Å.[10]

The short range of the data set precludes a quantitative analysis from a Fourier transform (FT) [4,11] solely of the experimental data. Nevertheless, the FT, over this same energy range, of theoretical curves for a series of $d_\perp$ values yields a single strong peak at a position that varies monotonically with $d_\perp$. When this peak position is treated semiempirically, the FT can be regarded as a compact parameterization of the NPD curve, and compared to the experimental FT curve. This approach yields $d_\perp$ =0.8(2) Å (Fig. 1D) in agreement with the above result.

As a check of the objectivity of our comparisons, an R-factor analysis,[9,12] normalized to the Zanazzi-Jona R-factor,[13] was performed. It yielded an absolute minimum (R_N= 0.16) for the hollow site geometry, $d_\perp$ = 0.8Å, and two relative minima at hollow site, $d_\perp$ = 0.1Å (R_N= 0.21) and bridge site, $d_\perp$ = 1.5Å (R_N= 0.23). The sensitivity of the method is borne out by the tremendous difference in the quality of the fits, as is shown in Fig. 2a-d. The only suitable

match is for the 0.8Å, hollow site, which is also the only curve with R_N less than 0.20, the value proposed by Zanazzi and Jona as an upper limit on a good fit. This is convincing evidence to support the emphasis placed upon this value and strongly suggests that this may be the method of choice for such comparisons.

The hollow site R-factors are depicted in Fig. 1C. The raw R-factor values were stable against variations in the inner potential (V_0) over the range of V_0 = 8eV to V_0 = 13eV. The slope of the R-factors near the absolute minimum, as well as the R-factor values at 0.7Å and 0.9Å, permits an error estimate of $d_\perp$ = 0.80(5)Å.

Addition of more oxygen to convert the c(2x2) structure to the $\sqrt{2}$ x $2\sqrt{2}$ structure added the expected new spots to the LEED pattern while sharpening those of the c(2x2) sublattice. The NPD curve showed little change, except at the lowest kinetic energies. It is therefore likely that the $\sqrt{2}$ x $2\sqrt{2}$ structure is formed by adding something less than 50% more oxygen to the c(2x2) lattice without otherwise substantially changing it. Figure 1B represents one of two orthogonal domains that can be formed in this way. Steric effects would appear to preclude any but the empty fourfold hollow sites for the new oxygen atoms. Electrostatic repulsion would hinder an arrangement with all of the oxygens in the same plane above the surface. Perhaps the new oxygens occupy positions at lower $d_\perp$ values, and the $\sqrt{2}$ x $2\sqrt{2}$ structure represents the initiation of the nucleation involved in surface oxidation. This might explain the low $d_\perp$ value found by Kono, et al.,[1] particularly in light of the special sensitivity of azimuthal photoelectron diffraction to near coplanar

species.[14]

Because local scattering effects dominate in NPD, we attempted to simulate the $\sqrt{2}$ x $2\sqrt{2}$ experimental curve by adding to the c(2x2) hollow, $d_\perp$ = 0.8 Å curve (taken to represent the "old" oxygens) various other c(2x2) theoretical curves (for the "new" oxygens) with relative weights 2:1. Two such composite curves are depicted in Fig. 2, for the 0.1 Å hollow site and the 1.5 Å bridge site. Both improve the agreement with experiment, but because of the overall similarity of the four curves (Fig.2e-h) and the foregoing discussion, our only firm conclusion about the $\sqrt{2}$ x $2\sqrt{2}$ structure is that it is dominated by the c(2x2) sublattice, in the hollow site, $d_\perp$ =0.8 Å geometry.

Note added after submission for publication:

Bauschlicher et al.[15] recently completed a self-consistent-field calculation of the interplanar spacing in a Cu_5O model cluster, with the result of $d_\perp$ = 0.9 Å, hollow. Moreover, they argue that $d_\perp$ = 0.8 Å is the optimum prediction.

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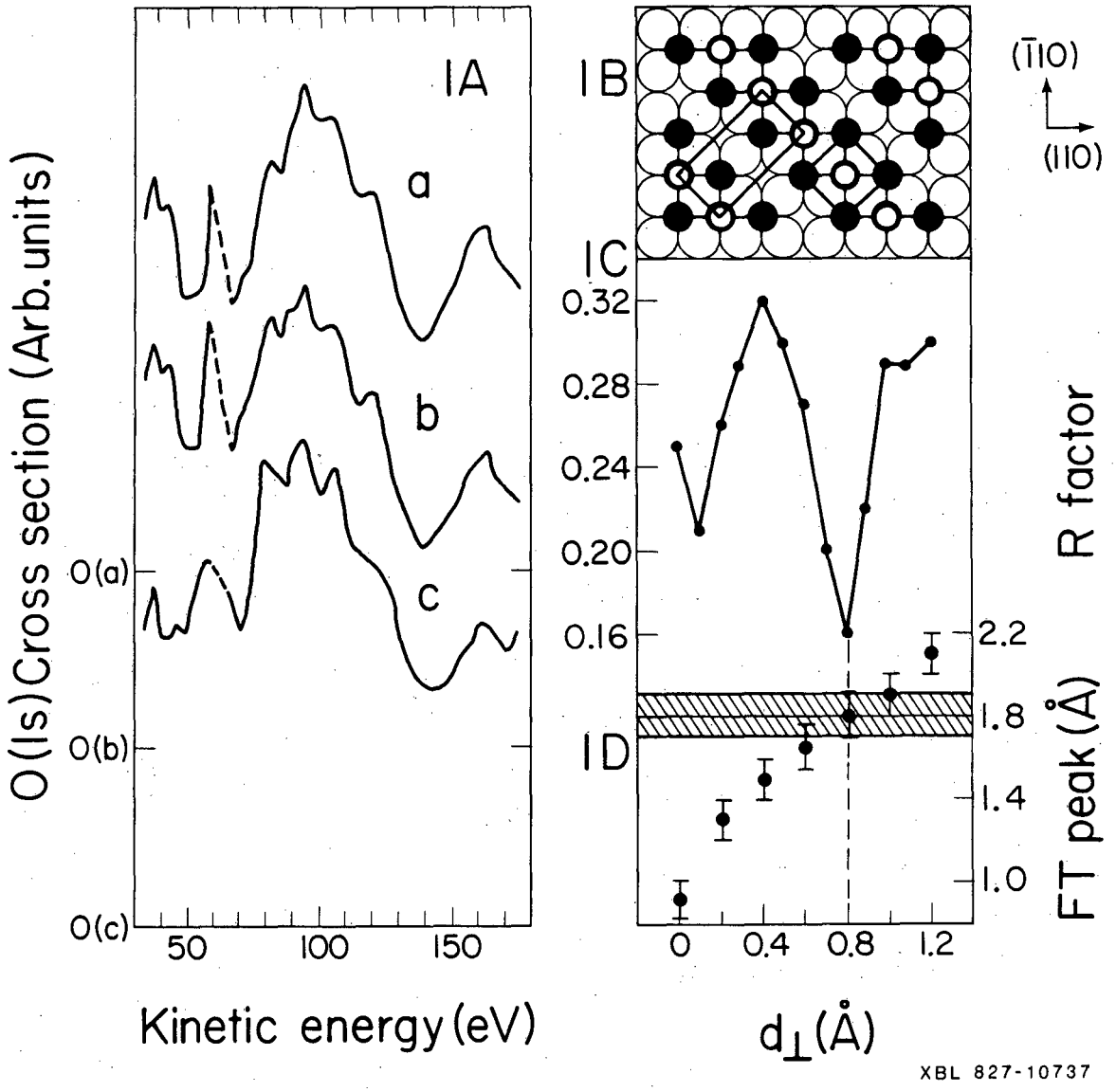
Figure Captions

Figure 1A. Experimental O(1s) cross section measurements: (a) c(2x2)O/Cu(001) in which the photon intensity normalization is made using the I_0 measurement from a gold grid-channeltron assembly; (b) same as (a) but with an internal photon intensity measurement made by sampling electrons at a KE above the O(1s) peak; (c) $(\sqrt{2} \times 2\sqrt{2})R45^\circ$ O/Cu(001), with normalization done as in (b). The dashed sections are interpolated values. The photoemission peaks at 61 and 64 eV were obfuscated by the Cu MVV Auger line.

Figure 1B Model of the Cu(001) surface (light circles) with the c(2x2) oxygens in the fourfold hollows (filled circles) and the additional $(\sqrt{2} \times 2\sqrt{2})$ oxygens also in the hollows (dark circles). Note the differences in the unit cells. Only one of two orthogonal domains is shown for the $(\sqrt{2} \times 2\sqrt{2})$ structure.

Figure 1C,D (C) R-factors (R_N) of the hollow site, normalized to the Zanazzi-Jona R-factor, showing a relative minimum at 0.1 Å and an absolute minimum at 0.8 Å (V_0= 10eV); (D) The position of the theory Fourier Transform (FT) peak, plotted against $d_\perp$, using no scattering-atom phase shifts. The experimental FT peak position is 1.8(1) Å: the theoretical FT peak has this value for $d_\perp$ = 0.8(2) Å, in agreement with the position of the absolute minimum in (C).

Figure 2. NPD experiment and theory for c(2x2)O/Cu(001): (a) experiment, same as Figure 1a; (b) theory, $d_\perp$ = 0.8 Å, hollow, R_N=0.16; (c) theory, $d_\perp$ =0.1 Å, hollow, R_N=0.21; (d) theory, $d_\perp$ = 1.5 Å, bridge, R_N=0.23. V_o = 10 eV. NPD experiment and theory for ($\sqrt{2}$ x $2\sqrt{2}$)R45° O/Cu(001): (e) experiment, same as Fig. 1c; (f) theory, $d_\perp$ =0.8 Å, hollow for c(2x2), R_N=0.21; (g) theory, 1:1/2 weighted sum of 0.8 Å hollow and 0.1 Å hollow, c(2x2) calculations, R_N=0.18; (h) theory, 1:1/2 weighted sum of 0.8 Å hollow and 1.5 Å bridge, c(2x2) calculations, R_N=0.15. V_o = 10 eV.


IA
a
b
c
O(a)
O(b)
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O(1s)Cross section (Arb.units)
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150
Kinetic energy(eV)
IB
IC
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(1̄10)
(110)
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0.28
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0.4
0.8
1.2
d⊥(Å)
R factor
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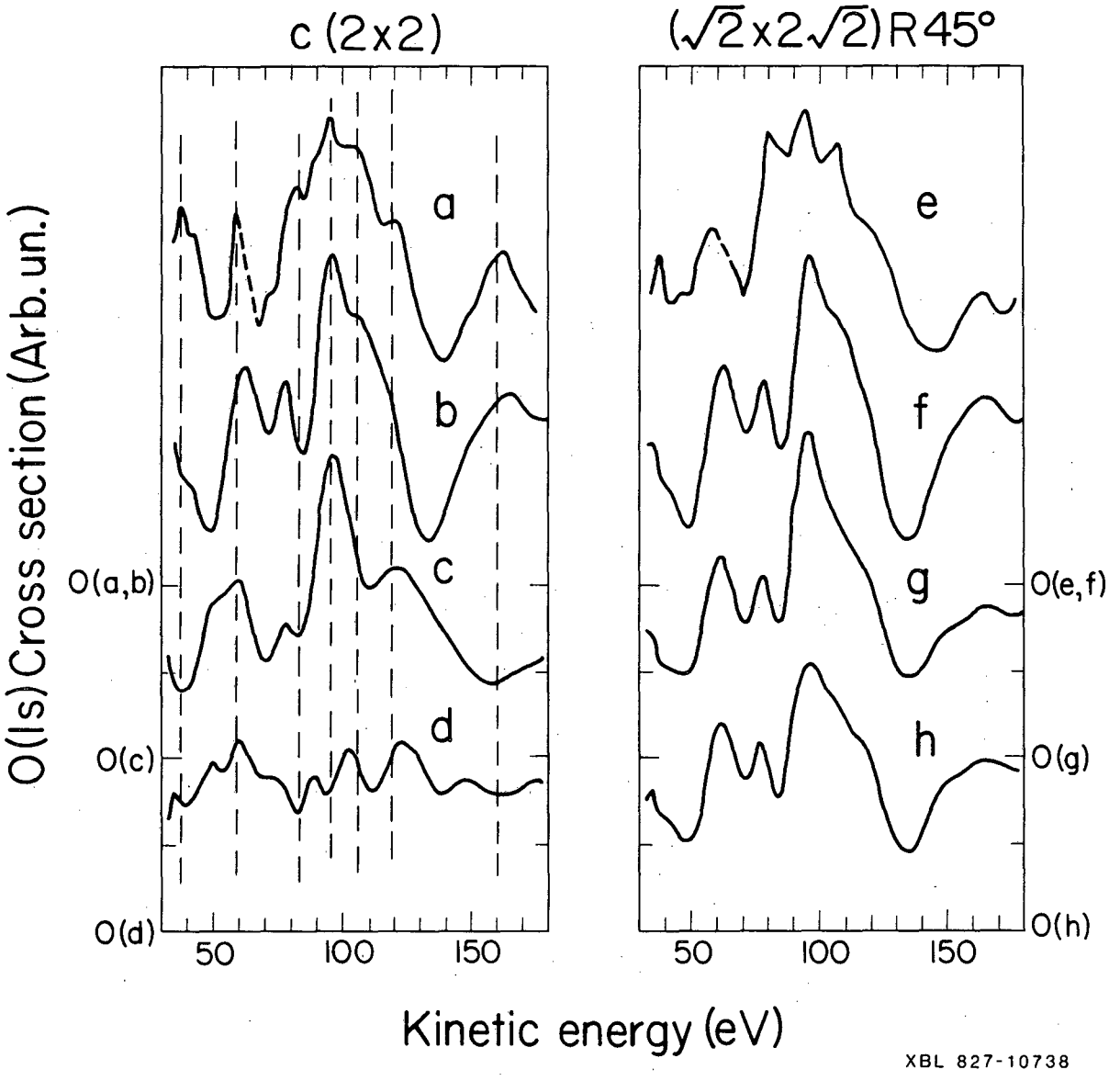
1.8
1.4
1.0
FT peak (Å)
XBL 827-10737

Figure 1


c (2x2)
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O(ls) Cross section (Arb. un.)
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O(g)
O(h)
50
100
150
50
100
150
Kinetic energy (eV)
XBL 827-10738

Figure 2

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