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Structure of $c(2\times 2)$ oxygen on Cu(100): A surface extended x-ray absorption fine-structure study

U. Döbler and K. Baberschke
Institut für Atom- und Festkörperphysik, Freie Universität Berlin, D-1000 Berlin 33,
Federal Republic of Germany

J. Stöhr
Corporate Research Science Laboratories, Exxon Research and Engineering Company,
Annandale, New Jersey 08801

D. A. Outka
Department of Chemical Engineering, Stanford University,
Stanford, California 94305

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The adsorption of oxygen on the Cu(100) face has been investigated by surface extended x-ray absorption fine-structure measurements for the low-coverage $(\sqrt{2}\times\sqrt{2})R45$ structure. The oxygen is found to occupy the fourfold hollow site with a bond length of 1.94(4) Å.

Here we report surface extended x-ray absorption fine-structure (SEXAFS) studies of the chemisorption geometry of oxygen on Cu(100). Our investigation was motivated by numerous conflicting experimental results and the availability of advanced theoretical calculations for this system.

All previous authors agree on the development of a $c(2\times 2)$ [hereafter referred to as $(\sqrt{2}\times\sqrt{2})R45$] superstructure in low-energy electron diffraction (LEED) at low coverages. However, no consensus has been reached up to date on the local adsorption geometry of the oxygen atom. Three main models have been proposed. (i) A reconstructed surface layer with alternating Cu and O atoms from a LEED study.[1,2] (ii) A bridge site 1.4 Å above the first Cu layer also from LEED.[3,4] (iii) A hollow site with various vertical spacings d between the O and the top Cu layer: $d\sim 0$ Å from azimuthal photoelectron diffraction (APD),[5-7] $d=0.8$ Å from normal photoelectron diffraction,[8] and $d=1.2$–1.5 Å from angle-resolved secondary-ion mass spectrometry (ARSIMS).[9] Most recently, within the same year a bridge site was claimed from the analysis of the LEED spot shape,[10] LEED intensity measurements were found to support a coplanar fourfold hollow (FFH) site,[11] and a FFH site with $d\sim 0.9$ Å was predicted by *ab initio* cluster calculations.[12] In addition, in some investigations[3,4,9] mixtures of adsorption of above plane and in plane hollow sites and/or above plane bridged and in plane hollow sites have been discussed.

Here, we present a polar-angle dependent SEXAFS study of the early chemisorption state of oxygen on Cu(100) characterized by a $(\sqrt{2}\times\sqrt{2})R45$ LEED pattern. These experiments clearly favor the hollow site adsorption with a bond length of 1.94(4) Å corresponding to a O-Cu layer spacing of 0.70(12) Å.

The experiments were performed using the SX-700 monochromator at the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY) and the grasshopper monochromator on beam line *I*-1 at the Stanford Synchrotron Radiation Laboratory (SSRL). Spectra were recorded by means of partial electron yield detection[13,14] for polar angles of $\theta=90°$ and $\theta=45°$ where θ is the angle between the **E** vector and the surface normal. The azimuthal angle was chosen such that at normal incidence the **E** vector was parallel to the [100] direction.

The samples were cleaned by argon bombardment at room temperature or at 300 °C and then annealed to 300 °C. No residual oxygen, sulfur, or carbon could be detected by Auger electron spectroscopy (AES) after this treatment. For the $(\sqrt{2}\times\sqrt{2})R45$ structure a dosage of 300 L O_2 (where 1 L $=10^{-6}$ Torr sec) at 300 K was used. No heat treatment was done to the covered sample. After annealing of a 600 L O_2 sample already weak spots of the second chemisorption state, the $(\sqrt{2}\times 2\sqrt{2})R45$ structure, could be observed, which were as intense as the half-order spots at 2000 L.

The literature exposures to obtain a sharp $(\sqrt{2}\times\sqrt{2})R45$ superstructure vary from 300 L used in this work, to 2100 L.[1] Also the crystal temperature is known to have a strong influence on the dosage that is needed to obtain a certain LEED pattern.[15] In order to minimize the effect of a possible mixture of the two known chemisorption states, a low exposure of 300 L and no annealing was used for the $(\sqrt{2}\times\sqrt{2})R45$ structure in the present study.

Figure 1 shows the SEXAFS spectra of oxygen on Cu(100) corresponding to a $(\sqrt{2}\times\sqrt{2})R45$ LEED pattern and for a single-crystal Cu_2O standard. The 300 L spectrum [$(\sqrt{2}\times\sqrt{2})R45$ structure] exhibits a shorter period as the Cu_2O standard corresponding to a longer O–Cu bond length.

Analysis of the SEXAFS data was performed using the conventional Fourier transform method as described elsewhere.[13] The dependence of the EXAFS amplitude on the angle between the absorber-backscatterer internuclear axis and the electrical field vector **E** yields the effect coordination number N^*. For a fourfold hollow site[13]

$$N^*=6(2\cos^2\theta\cos^2\beta+\sin^2\theta\sin^2\beta)\ , \qquad (1)$$

where β is the angle between the surface normal and the O-Cu internuclear axis.

Figure 2 shows the absolute Fourier transforms for $\theta=90°$ and 45° for the 300 L O/Cu(100) sample measured at

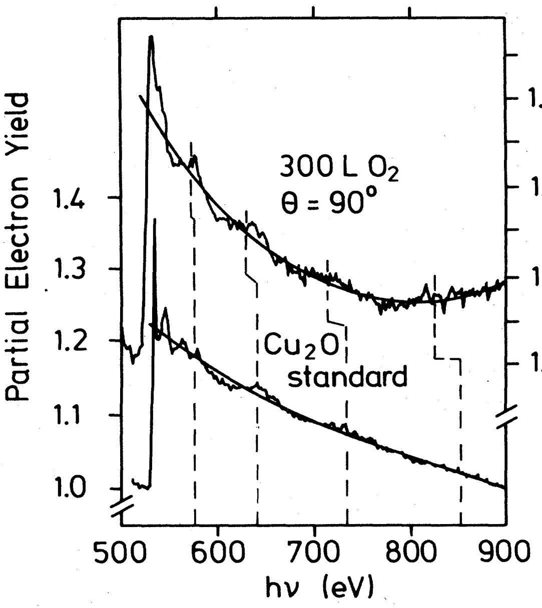

FIG. 1. Partical electron yield for 300 L O dosage and normal incidence as well as for the Cu_2O standard. Dashed lines indicate the EXAFS oscillation periods.

BESSY. Using the phase shift derived from the Cu_2O standard with a O-Cu distance of 1.85 Å, one determines a distance of 1.93(4) Å for normal incidence and 1.95(4) Å for $\theta=45°$ as summarized in Table I. For different samples, measured at BESSY and at SSRL the derived bond length was the same within 0.01 Å. The SEXAFS amplitude ratio $A(90°)/A(45°)$ derived for the 300 L sample is 1.4(2). Of the various previously suggested sites this only agrees with the oxygen sitting in a fourfold hollow site. Assuming the bulk lattice constant $a=3.615$ Å yields a vertical spacing of $d=0.70(12)$ Å.

The results on the $(\sqrt{2}\times\sqrt{2})R45$ structure are compared in Table II with different trial geometries. The reconstruction model[1,2] with alternating oxygen and copper atoms nearly in plane corresponds to a bond length of 2.55 Å which can clearly be ruled out. For the bridge adsorption as proposed in Refs. 3, 4, and 10 with a O–Cu bond length of 1.90 Å one calculates using Eq. (1) a theoretical amplitude ratio $A(90°)/A(45°)$ of 0.6, which is clearly outside our error bar. In Ref. 3, LEED intensity data are compared with dynamical calculations for two fourfold hollow site positions only, corresponding to $d=0.2$ and 0.9 Å. The calculated curves vary strongly between these two sites and our result of $d=0.7$ Å falls in between the calculated cases. The fourfold hollow site with $d=1.2$–1.5 Å claimed in Ref. 9 using ARSIMS data has to be questioned because of missing LEED capabilities, and the used exposure of 1200 L oxygen could already have resulted in a large fraction of the $(\sqrt{2}\times2\sqrt{2})R45$ structure. A 1.2–1.5 Å vertical spacing in a fourfold hollow site corresponds to a bond length of 2.17–2.35 Å which is much longer than a typical O-Cu distance of ~1.9 Å as in CuO (1.95 Å) and Cu_2O (1.85 Å). APD data[5-7] supported a coplanar ($d\sim0$ Å) fourfold hollow site. This corresponds to a bond length of 1.81 Å and yields a calculated amplitude ratio of 2.0. Both values are clearly outside the error bar of the SEXAFS data for the $(\sqrt{2}\times\sqrt{2})R45$ structure. This discrepancy could be explained as follows. Extra features of the $(\sqrt{2}\times2\sqrt{2})R45$ structure start to develop already at 600 L O and also during long measurements on the same sample.[3,8] Since no *in situ* LEED capabilities existed in the APD studies a possible mixture of the two adsorption sites could have been present. This would have affected the measured diffraction pattern,

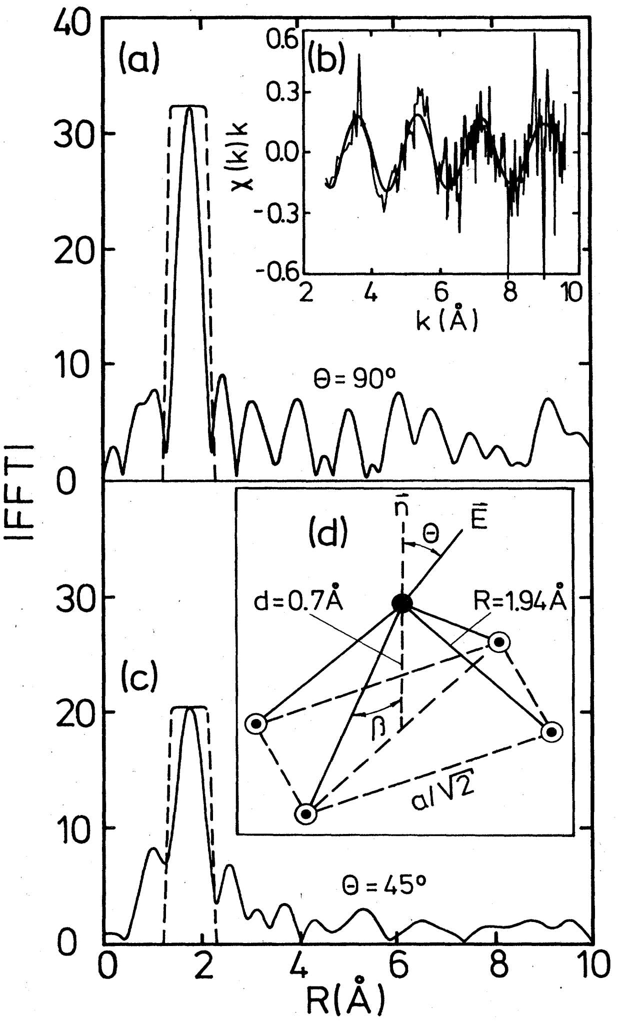

FIG. 2. Absolute Fourier transforms for normal ($\theta=90°$) (a) and ($\theta=45°$) (c) incidence [the angles and crystal orientations are defined in the lower insert (d)]. The dashed line is the filter that is used for back transformation. In the upper insert (b) $\chi(k)k$ and the filtered back transform is shown for $\theta=90°$. The lower insert (d) shows the proposed model structure (nearest-neighbor configuration).

TABLE I. Experimental values for the bond length and amplitude ratios for $(\sqrt{2}\times\sqrt{2})R45$ O on Cu(100) (300 L at 300 K). The theoretical ratio is calculated for a fourfold hollow site using Eq. (1).

	Experimental			Theoretical
θ (deg)	R (Å)	d (Å)	$A(90)/A(45)$	$A(90)/(45)$
90	1.93(4)	0.70(8)	1.4(2)	1.5
45	1.95(4)			

TABLE II. A comparison of the present results for the $(\sqrt{2}\times\sqrt{2})R45$ structure with other work.

Experimental			Theoretical		
R (Å)	d (Å)	$A(90°/A(45°)$	$A(90°)/A(45°)$	Site	Ref.
1.94	0.70(12)	1.4(2)	1.5	Hollow	This work
2.55	0.0		2.0	Reconstructed	1,2
1.90	1.4		0.6	Bridge	3,4
2.35	1.5		0.8	Hollow	9
1.81	0.0		2.0	Hollow	5,6,7,11
1.97	0.80(5)		1.4	Hollow	8

possibly in the way suggested in Ref. 8. In a recent LEED study[11] only calculations for the deep fourfold hollow site were done. They yielded reasonable agreement to their experimental data, but no other trial models have been investigated.

Although we tried to avoid having any mixture of the $(\sqrt{2}\times\sqrt{2})R45$ and $(\sqrt{2}\times 2\sqrt{2})R45$ as verified by LEED, a hypothetical upper limit for an additional adsorption site (in $d=0.1$ Å FFH or $d=1.4$ Å bridge site) is about 30%.

Our results are compatible with only one other experimental structure determination, namely, the normal photoelectron diffraction studies,[1] which favored a FFH site with $d=0.80(5)$ Å corresponding to a O-Cu distance of 1.97(3) Å. It also agrees with recent *ab initio* cluster calculations[12] which predicted a FFH chemisorption site with $d\sim 0.9$ Å, although our experimental value for d is somewhat smaller. The close correspondence between the $(\sqrt{2}\times\sqrt{2})R45$ oxygen chemisorption phase on Cu(100) with that on Ni(100) suggested by theory[12] is strongly supported by the present study. The chemisorption sites are the same for both systems and even the bond lengths are almost identical, 1.94(3) Å for O/Cu(100) as compared with 1.96(3) Å for O/Ni(100).[16]

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