Surface Extended X-Ray-Absorption Fine-Structure Study of the O(2×1)/Cu(110) System: Missing-Row Reconstruction, and Anisotropy in the Surface Mean Free Path and in the Surface Debye-Waller Factor

M. Bader, A. Puschmann, C. Ocal,[a] and J. Haase
Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33, West Germany
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Polarization-dependent surface extended x-ray-absorption fine-structure (SEXAFS) measurements on the O(2×1)/Cu(110) system show that every second [001] Cu row on the surface is missing, thus excluding the buckled-row model for the reconstruction. A SEXAFS amplitude comparison clearly favors the missing-row over the sawtooth model. It also provides evidence for a strong anisotropy of both the surface mean free path and the surface Debye-Waller factor.

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Atomic oxygen in the (2×1) overlayer on Cu(110) was found to be absorbed in the long bridge site with the oxygen atoms about 0.3 Å above the surface.[1] Various experimental techniques have established a reconstruction in the oxygen-covered surface, involving the removal or a displacement of every second [001] row in the first layer. However, whereas low-energy ion scattering,[2] He-beam diffraction,[3] and impact-collision alkali-ion scattering[4] studies favor a missing-row model (with every second [001] Cu row missing) for the reconstruction, high-energy ion scattering,[5] angle-resolved photoemission,[6] and grazing-incidence x-ray scattering[7] results indicate a buckled-row model (with every second [001] Cu row displaced vertically). The sawtooth model (rotated by 90° with respect to the original model of Bonzel and Ferrer[8]) has also been discussed in this context.[4] In our earlier oxygen-K-edge surface extended x-ray-absorption fine-structure (SEXAFS) study[1] the adsorption site was unambiguously determined, but no information on surface reconstruction could be obtained. Having improved the experimental conditions mainly by using the monochromator with a new holographic grating with higher suppression of second orders we have now reinvestigated the O(2×1)/Cu(110) system. The data now allow the determination of fourth-nearest-neighbor distances and show that third-nearest Cu neighbors are definitely absent. A buckled-row reconstruction model is thus excluded. This is the first SEXAFS study in which bond-length measurements alone prove reconstruction of an adsorbate-covered surface. An additional amplitude comparison clearly favors a missing row over a sawtooth reconstruction model.

The EXAFS amplitude contains two exponential damping terms due to Debye-Waller-like effects and due to inelastic scattering of the emitted and backscattered photoelectrons with a mean free path, λ. Both have to be taken into account in amplitude comparisons. Anisotropies in the Debye-Waller factor and the mean free path are then a serious problem.[9] Recently an anisotropy in the surface Debye-Waller factor has in fact been established.[10] Mean free paths, however, have not yet been extracted from SEXAFS measurements. Where appropriate, averaged bulk values[11] have been used.[12] Our data show for the first time that the surface mean free path is anisotropic. The energy-averaged value of λ for electron propagation from the adsorbed oxygen to the second- and fourth-nearest Cu neighbors down in the bulk, $\lambda_{SB}=5.2$ Å, is much smaller than that for electron propagation from the oxygen to the nearest Cu neighbors on the surface [$(\lambda_{SS}-\lambda_{SB})=1.4$ Å].

The experiments were conducted at the Berlin electron storage ring BESSY with the grazing-incidence plane grating monochromator SX-700[13] by use of a 1200-lines/m holographic grating. The data were taken in the partial electron yield mode with a four-grid high-pass filter combined with a channelplate multiplier as a detector,[14] which was set to a retarding voltage of -400 V. The spectra shown are the ratio covered to clean. They were analyzed by the conventional Fourier transform method (see Ref. 1 and references therein). The Cu crystal was prepared and characterized as before.[1] The surface was exposed to oxygen at room temperature, whereas the measurements were performed at 100 K.

The oxygen-K-edge SEXAFS spectra taken for normal incidence ($\theta=90°$), with the **E** vector in the [001] and [1$\bar{1}$0] azimuths, are shown in Fig. 1 together with their Fourier transforms. A third spectrum taken in [1$\bar{1}$0] for $\theta=45°$ was similar to the $\theta=90°$ spectrum and is not shown. Peaks A, C, and D correspond to the first (R_1), second (R_2), and fourth (R_4) nearest-neighbor distances, respectively. They are schematically shown in Fig. 2. R_4 is a superposition of three close lying distances from the O atoms to Cu atoms in the second and third layers. The measured R_i values are listed in Table I, column 4.

Third-nearest Cu neighbors with $R_3\sim3.14$ Å are *not* seen in the Fourier transform of the SEXAFS spectra taken in the [1$\bar{1}$0] azimuth. As the SEXAFS amplitude is proportional to an R^2-weighted effective coordination number N^* (see below), we calculated N_i^*/R_i^2 values for

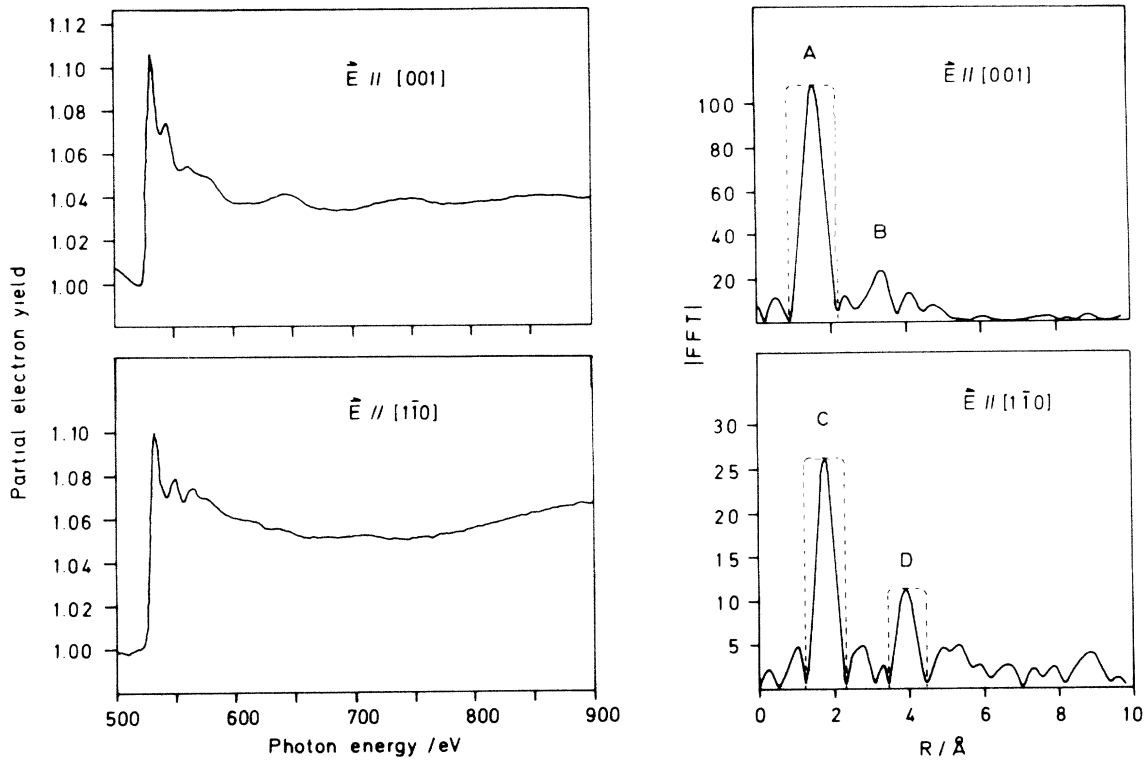

FIG. 1. Oxygen-K-edge SEXAFS spectra for O(2×1)/Cu(110) recorded at 100 K with $\mathbf{E} \parallel [001]$ and $\mathbf{E} \parallel [0\bar{0}1]$ (left), and their Fourier transforms (right). For peak notation see text.

all Cu neighbors assuming the adsorption geometry discussed above. They are listed in Table I, column 7. A comparison of these numbers shows that if third-nearest Cu neighbors were present, the amplitude of their Fourier peak should be larger than those of the second- and fourth-nearest neighbors in contrast to the experimental result. Hence, the oxygen-covered Cu(110) surface is clearly reconstructed. The reconstruction models which are presently discussed in the literature are shown in Fig. 2. In the buckled-row model[5] every second [001] Cu row is shifted outward by roughly 0.3 Å from its bulk position. Our measured bond lengths agree with this model only if the oxygen atoms sit above the unshifted [001] rows. Third-nearest Cu neighbors, however, should then be observed at a distance of 3.14 Å, and this value will be increased only slightly when the outward shift is much bigger than 0.3 Å. From the fact that no peak appears in the Fourier transform around 3.2 Å and no unexplained peak exists in all the Fourier transforms we conclude that the non-oxygen-containing [001] Cu rows are definitely missing and unambiguously rule out any other reconstruction in the top layer.

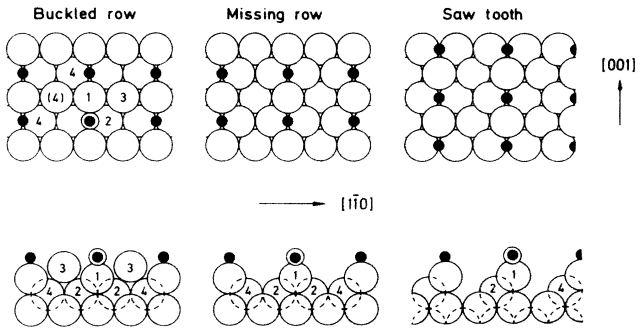

FIG. 2. Reconstruction models for O(2×1)/Cu(110). In the top view of the buckled-row model and in all side views the nearest-neighbor numbering with respect to the absorbing O atom (circled dots) is shown. The notation (4) corresponds to the Cu atom in the third layer.

The missing-row (MR) and sawtooth (ST) reconstruction models only differ in the number of second- and fourth-nearest neighbors (cf. Fig. 2). To decide between the MR and the ST model we thus have to resort to amplitude comparisons. The generally accepted form of the EXAFS amplitude for a shell i in which all backscattering atoms have the same distance R_i from the absorbing atom is given by[15]

$$A_i(k) = \frac{N_i^*}{kR_i^2} F_i(k) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda_i(k)}, \qquad (1)$$

where k denotes the photoelectron wave number, $F_i(k)$ the backscattering amplitude, and σ_i^2 the temperature-dependent mean-square relative displacement. The

TABLE I. Experimental and theoretical bond lengths and amplitude ratios. The theoretical values were calculated assuming the oxygens 0.25 Å above the surface. The measured distance R_2 for $\theta=45°$ has a slight contribution from R_1 and is therefore smaller than $R_2=90°$. The amplitude of peak 4 for $\theta=45°$ could only be approximated by the height of the Fourier transform. We therefore did not use the 45° measurement for the determination of λ_{SB} (see text).

			Experiment		Theory $\frac{N_i^*/R_i^2}{N_1^*/R_1^2}$			
Azimuth	θ/degrees	Cu neighbor	R_i (Å)	A_i/A_1 ($k=4$ Å^{-1})	R_i (Å)	No reconstruction	Missing row	Sawtooth
[001]	90	1	1.82 ± 0.02	1	1.83	1	1	1
[1$\bar{1}$0]	90	2	1.99 ± 0.02	0.28 ± 0.01	1.99	0.355	0.355	0.178
		3	. . .	. . .	3.14	0.458	. . .	. . .
		4	4.15 ± 0.03	0.12 ± 0.01	4.16	0.354	0.354	0.251
[1$\bar{1}$0]	45	2	1.97 ± 0.02	0.31 ± 0.01	1.98	0.441	0.441	0.220
		4	4.21 ± 0.05	0.10 ± 0.03	4.17	0.304	0.304	0.231

mean free path $\lambda_i(k)$ is a convolution of the mean free path of the photoelectron traveling from the absorbing atom to the backscattering atoms in the ith shell (and back) and the lifetime of the core hole.[11] Normally λ is dominated by the photoelectron.[11] The logarithm of an amplitude ratio A_i/A_j is then

$$\ln[A_i(k)/A_j(k)]=\ln\frac{N_i^*/R_i^2}{N_j^*/R_j^2}-2(\sigma_i^2-\sigma_j^2)k^2 - 2[R_i/\lambda_i(k)-R_j/\lambda_j(k)]. \quad (2)$$

The backtransforms of the Fourier peaks A, C, and D, using the dashed windows shown in Fig. 1, yielded the SEXAFS amplitudes A_1, A_2, and A_4, respectively, as a function of k. Amplitude ratios A_i/A_1 at $k=4$ Å^{-1} are listed in Table I, column 5. Figure 3 shows the logarithms of the amplitude ratios A_4/A_2 and A_2/A_1, which we discuss separately:

(a) A_4/A_2: With the assumption that $\lambda_4=\lambda_2=\lambda_{SB}$, the k-dependent terms in Eq. (2) are

$$-2(\sigma_4^2-\sigma_2^2)k^2-2(R_4-R_2)/\lambda_{SB}(k).$$

The fact that the experimental $\ln(A_4/A_2)$ is linear in k^2 suggests that there is only a weak k dependence of λ_{SB} in agreement with the only known bulk EXAFS-derived values for $\lambda(k)$.[11] The measured $\Delta\sigma^2=\sigma_4^2-\sigma_2^2=2.1\times10^{-3}$ Å^2 results from the distance-dependent correlation of the motion of the corresponding atoms.[16] It is in reasonably good agreement with $\Delta\sigma^2=1.7\times10^{-3}$ Å^2 calculated according to the Debye model with the bulk Debye-Waller factor for Cu as input.[16] Fitting the experimental A_4/A_2 to the theoretical one and taking into account the Debye-Waller correction (6% at $k=4$ Å^{-1}) will yield the mean free path λ_{SB}.

(b) A_2/A_1: With the assumption that for simplicity $R_1=R_2=R$ the k-dependent terms in Eq. (2) with $\lambda_1=\lambda_{SS}$ and $\lambda_2=\lambda_{SB}$ are then $-2(\sigma_2^2-\sigma_1^2)k^2-2R[\lambda_{SS}(k)-\lambda_{SB}(k)]/\lambda_{SS}(k)\lambda_{SB}(k)$. The experimental $\ln(A_2/A_1)$ is linear in k^2 for both measurements in the [1$\bar{1}$0] azimuth, which again indicates only a slight k dependence of λ_{SS} and λ_{SB}, if there is any at all. The measured $\Delta\sigma^2=\sigma_2^2-\sigma_1^2=2.4\times10^{-3}$ Å^2 is representative for the anisotropy of the surface Debye-Waller factor. It means that $\sigma_2=\sigma_{SB}$ is bigger than $\sigma_1=\sigma_{SS}$ in agreement with recent measurements on the Co/Cu(111) system.[10] This result is expected because, among other reasons, the oxygen bonds primarily to the surface Cu atoms, and thus there is a larger correlation between their motions than between the motions of the O atoms and the Cu atoms in the second layer. Our $\Delta\sigma^2$ is roughly twice the value found for the Co/Cu(111) system. Taking into account this Debye-Waller correction (7% at $k=4$ Å^{-1}) the experimental amplitude ratios still do not fit the theoretical ones (neither for the MR, nor for

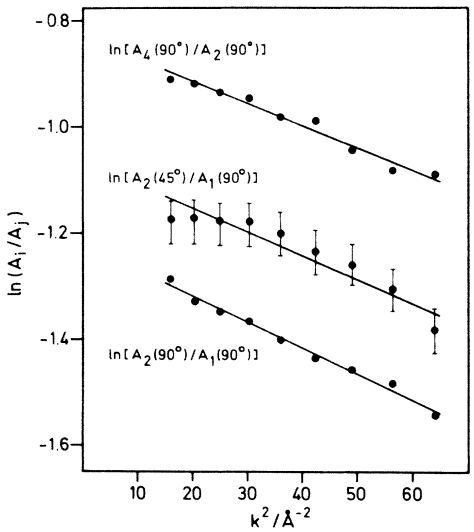

FIG. 3. Logarithm of different SEXAFS amplitude ratios as a function of k^2. Amplitudes A_1 have been measured in the azimuth [001] and amplitudes A_2 and A_4 in the azimuth [1$\bar{1}$0] for different polar angles θ (given in parentheses).

the ST model). The surface mean free path thus appears to be anisotropic: $\lambda_{SS} \neq \lambda_{SB}$. According to the jellium model,[17] because of the decreasing electron density at the surface, λ_{SS} is expected to be larger than λ_{SB}.

A comparison of column 5 with columns 8 and 9 of Table I tells us that with $\lambda_{SS} > \lambda_{SB}$ our experimental (A_2/A_1) values can only be fitted to the MR model, whereas for $\lambda_{SS} < \lambda_{SB}$ only the ST model can be appropriate. Assuming now the MR model to be valid we determine from A_4/A_2 an energy-averaged $\lambda_{SB} = 5.2 \pm 0.5$ Å and from A_2/A_1 an average $\Delta\lambda = \lambda_{SS} - \lambda_{SB} = 1.4 \pm 0.4$ Å. The λ_{SB} value is in excellent agreement with the only known bulk EXAFS-derived mean free paths which all center around 5 Å[11]; a $\Delta\lambda$ of the measured size has already been expected.[9] Fitting the experimental amplitude ratios to the ST model would result in $\lambda_{SB} = 3.7$ Å and $\lambda_{SS} = 1.4$ Å ($\Delta\lambda = -2.3$ Å). Besides the fact that $\lambda_{SS} < \lambda_{SB}$ is physically unreasonable, the absolute values are too low. Therefore, the data unambiguously rule out the ST model in agreement with impact-collision alkali-ion-scattering results.[4]

In summary, our experiments clearly show by bond-length determination only that every second [001] Cu row in the oxygen-covered Cu(110) surface is missing. SEXAFS amplitude comparisons unambiguously favor the missing-row over the sawtooth reconstruction model and reveal anisotropies in the surface Debye-Waller factor and the surface mean free path.

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[a]Permanent address: Departamento de Física Fundamental, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain.

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