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Oxygen chemisorption on Cu(110): A structural determination by x-ray diffraction

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A structural determination of the Cu(110)2×1-O surface has been performed by x-ray diffraction. Because of the simplicity of the structure, all structure factors are real and positive, and so a Fourier transform of the structure-factor intensities provides the electron-density map directly. The surface has a first layer of copper with half the (001) rows missing and oxygen atoms located in a long-bridge position 0.34 ± 0.17 Å below the surface. The missing-row layer is displaced outwards by 0.37 ± 0.05 Å relative to an ideally terminated crystal. The second copper layer has a small lateral displacement of 0.031 ± 0.005 Å towards the missing rows.

The chemisorption of oxygen on metal surfaces is an important step in such fundamental processes as catalysis or corrosion. A knowledge of the atomic structure is necessary to understand these processes in detail. In many cases where the structure has been studied, it is still a matter of controversy. Oxygen on the Cu(110) surface is such an example. It has been known since the work of Ertl over twenty years ago[1] that adsorption of half a monolayer of oxygen on the surface induces a 2×1 structure. However, there is still an ongoing debate as to whether or not the copper surface has a missing-row reconstruction and where the oxygen is located (for a historical review see Ref. 2). Briefly, the missing-row (MR) structure, where every second (001) row on the surface is absent (see Fig. 1), was proposed by de Wit and Bronckers on the basis of low-energy ion-scattering (LEIS) experiments.[3] The model was later supported by other groups using the LEIS technique,[4,5] and also by surface-extended x-ray-absorption fine-structure measurements.[6] On the other hand, high-energy ion scattering[7] and, very recently, scanning tunneling microscopy (STM),[8] provide contradictory data and favor a buckled-row model in which every second row of (001) copper atoms is not missing but shifted outwards. All studies[2-8] seem to agree that the oxygen is located in a long-bridge position in every second (001) row (see Fig. 1), but disagree on whether the oxygen atom is above or below the first layer of copper (see Ref. 2).

X-ray diffraction has, over the last five years, proven to be a powerful technique for determining the structure of surfaces[9] and should be well-suited for settling the above-mentioned controversy. Furthermore, the Cu(110)2×1-O system can serve as a prototype for the applicability for x-ray diffraction to study light elements adsorbed on metal surfaces. In addition to determining the reconstruction of the copper surface, we demonstrate how x-ray diffraction can directly locate the chemisorption site of the oxygen atom.

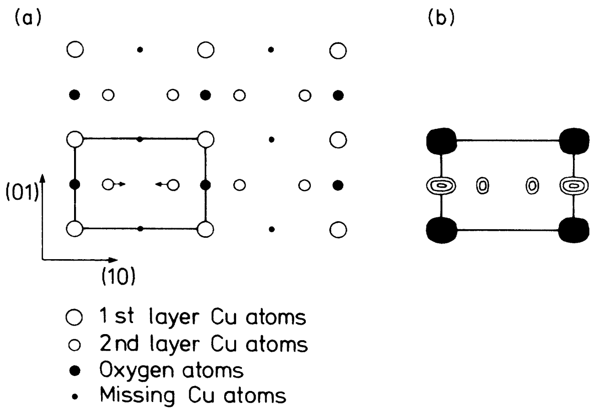

FIG. 1. (a) Top view of the missing-row structure of Cu(110)2×1-O proposed by de Wit *et al.* (Ref. 3). The square is the unit cell shown in (b). The arrows on the second-layer atoms mark the directions of their displacements. (b) A contour plot of the electron density using the fractional-order structure factors. The copper atom in the missing-row layer is located at the origin (raising ten contour levels), the oxygen is sitting at $(0, \frac{1}{2})$, and the second-layer is relaxed.

The x-ray diffraction measurements were performed at the 32-pole wiggler W1 beamline at the Hamburger Synchrotron Radiation Laboratory (HASYLAB). The Cu(110) crystal was purchased from Metal Crystal & Oxides Ltd., Cambridge, England. The crystal was 9 mm in diameter and mechanically polished to 1 μm. The surface had a 1.4° miscut along the [100] direction as determined by the x-ray diffraction measurements. The surface was prepared and characterized at the photoemission beamline FLIPPER II. It was cleaned by 500-eV Ar^+ ion bombardment and subsequently annealed to 430 °C. The 2×1 structure was produced by a dosage of 10 langmuir O_2 with an ion gauge close to the sample to activate the oxygen and thereby enhance the sticking coefficient. This was done at room temperature, but the 2×1 low-energy electron-diffraction (LEED) pattern was improved by briefly annealing to 400 °C. In fact, the 2×1 LEED pattern was sharper than that of the unreconstructed surface, suggesting that oxygen stabilizes large (110) terraces on the surface. This has also been seen by x-ray reflectivity measurements.[10] After preparation the sample was transferred to a portable x-ray UHV cell which was mounted on the vertical scattering diffractometer at beamline W1.[9] The x-ray wavelength was set to 1.40 Å, far enough away from the Cu K edge to avoid fluorescence. The surface was aligned by total external reflection in order to keep a fixed angle of incidence to the surface. The angle was set to 0.38°, the critical angle for total reflection. Integrated intensities were collected by rocking scans around the surface normal ("ω scans") with a wide open (0.5°) in-plane detector aperture. Out of plane the aperture corresponded to a resolution of 0.073 $\mathrm{Å}^{-1}$. The mosaic spread of the crystal was 0.7°. The domain size was at least 500 Å, as determined from radial scans. In total, integrated intensities were collected for 41 fractional-order and 14 integer-order reflections. Symmetry-equivalent reflections were averaged to obtain 15 fractional-order and 7 integer-order nonsymmetry equivalent intensities. The reproducibility between symmetry equivalents was to within ~5%. The integrated intensities were corrected for the Lorentz factor ($1/\sin2\theta$) and for variations in the active sample area ($1/\sin2\theta$) in order to obtain the structure-factor intensities.[9] The uncertainties were deduced from the reproducibility.[9] In the following, we will index the reflections with respect to a surface unit cell defined by $\mathbf{a}^*=(1\bar{1}0)_{\rm bulk}$, $\mathbf{b}^*=(001)_{\rm bulk}$, and $\mathbf{c}^*=(110)_{\rm bulk}$.

The pattern of the structure-factor intensities is shown in Fig. 2. The most striking feature is the weakness of the integer-order reflections which provide strong evidence for a missing-row structure. To show this, let us first consider the crystal truncation rods (CTR) for an ideal, unreconstructed surface.[11] The phase difference between subsequent (110) layers is $\Psi=\pi(h+k+l)$. The structure factor is obtained by summing up the contributions from the layers from a semi-infinite crystal,

$$F_{\rm CTR}=f_{\rm Cu}\sum_{n=1}^{\infty}e^{in\Psi}=\tfrac{1}{2}f_{\rm Cu}ie^{i\Psi/2}\frac{1}{\sin(\Psi/2)}\,, \qquad (1)$$

where $f_{\rm Cu}$ is the form factor for Cu. For in-plane ($l=0$) integer-order reflections, which are not bulk Bragg reflections, we get $F_{\rm CTR}=-\frac{1}{2}f_{\rm Cu}$. A half-filled surface layer with atoms at bulk lattice sites has $F_{\rm MR}=+\frac{1}{2}f_{\rm Cu}$. Hence, at the in-plane integer-order reflections the scattering from the missing-row layer is exactly canceled by the scattering from the truncation of underlying bulk. This explains why the in-plane integer-order reflections are so weak.

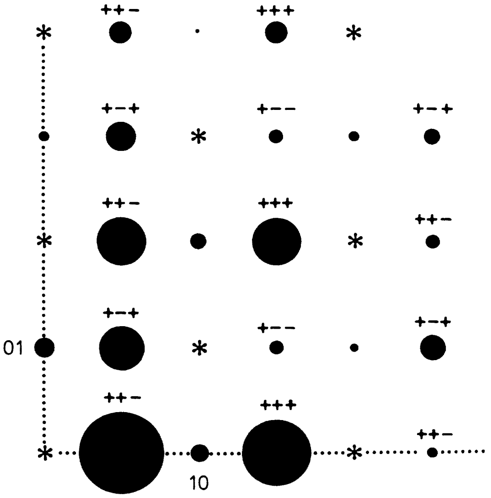

FIG. 2. The in-plane intensity pattern. The intensities are proportional to the areas of the circles. The asterisks mark the bulk Bragg points. The plus and minus signs denote when the different contributions in the structure are in phase and out of phase. The first sign is for the missing-row layer, the second for the oxygen, and the third for the second layer.

From Eq. (1) we can calculate the scattered intensity along the Bragg rods to be

$$I_{\rm CTR}=|F_{\rm CTR}|^2=\tfrac{1}{4}f_{\rm Cu}^2\frac{1}{\sin^2(\Psi/2)}\,,\quad \Psi=\pi(h+k+l)\,,$$
$$I_{\rm MR}=I_{\rm CTR}-\tfrac{1}{4}f_{\rm Cu}^2\,. \qquad (2)$$

These intensities are plotted in Fig. 3 for $(h,k)=(1,0)$ and (1,1). The scattered intensity for the (1,0) rod at $l=0.76$ (the maximum obtainable momentum transfer normal to the surface due to mechanical constraints in the present experiment) does not depend strongly on the details of the atomic structure at the surface. This allows us to tentatively put the measured intensities on an absolute scale. As seen, the experimental data fall between the curve for an ideally terminated surface (dashed-dotted curve) and the curve for a missing-row surface (dashed curve). The discrepancy is naturally explained by noting that the scattering at $l\approx0$ corresponds roughly to scattering from $\frac{1}{2}$ monolayer of oxygen on the surface[7] (marked by the arrow).

While the intensities of the in-plane integer-order reflections can be accounted for by a 2×1 structure with one copper and one oxygen atom per unit cell, details of the atomic positions are still lacking. These can be obtained from the in-plane fractional-order intensities if we assume that the symmetry of the bulk crystal is imposed onto the surface. In this case the structure projected onto the surface plane has a center of inversion. The in-plane structure factors are therefore real. Furthermore, because

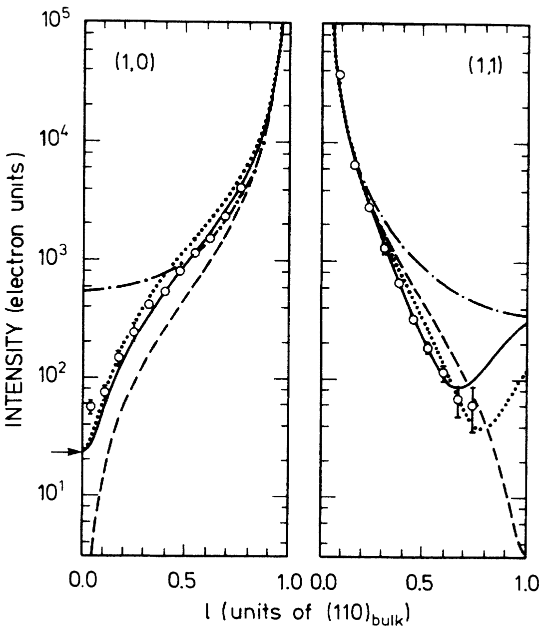

FIG. 3. Crystal truncation rods for $(h,k)=(1,0)$ and $(1,1)$. The dash-dotted curve corresponds to an ideally terminated crystal and the dashed curve corresponds to an ideally terminated crystal with a half-filled first layer. The solid curve is the best model with oxygen 0.34 Å below the outwards relaxed missing-row layer, whereas the dotted curve has oxygen 0.34 Å above the missing-row layer. The arrow on the (1,0) rod marks the scattering from $\frac{1}{2}$ monolayer of oxygen. The intensity is given as (electrons/2×1 cell)^2.

the copper atom in the unit cell is acting as a heavy atom and dominates the phases of the structure factors, the fractional-order structure factors must be positive. We can then directly plot the electron density

$$\rho(x,y)=\sum_{h,k}F_{hk}\cos[2\pi(hx+ky)]\,, \tag{3}$$

as shown in Fig. 1(b). Only fractional-order reflections are used and the contour plot only contains the parts of the surface with 2×1 periodicity.[9] Clearly, the structure has three components: (1) the missing-row structure with one copper atom at the origin, (2) one oxygen atom located at the $(0,\frac{1}{2})$ position, the long-bridge position, and (3) a lateral relaxation of the second-layer copper atoms towards the missing rows. The structure factors for each of these components can easily be calculated for half-order reflections

$$F_{hk}=\begin{cases} f_{\text{Cu}}\,, & \text{1st copper layer}\,,\\ (-1)^k f_{\text{O}}\,, & \text{oxygen}\,,\\ 2f_{\text{Cu}}(-1)^{h+k+1/2}\sin(2\pi\delta h)\,, & \text{2nd copper layer}\,, \end{cases} \tag{4}$$

where δ is the second-layer displacement in units of $\mathbf{a}^*$. Positive δ indicates displacements towards the missing row. This accounts for the variation in the intensities of the fractional-order reflections, as seen in Fig. 2. At small h, only the contribution from the missing-row layer and the oxygen atoms matter, and they scatter in phase or out of phase, depending on k. At larger h, the scattering from the relaxed second layer becomes important. The least-squares analysis has four free parameters: an overall scale factor, one thermal Debye-Waller factor for the missing-row layer, and one for the oxygen atom, and the displacement of the second layer. The Debye-Waller factor for the second and deeper layers is kept constant at the bulk value of $B=0.55$ Å^2 (Ref. 12).

The agreement is good. We obtain $\chi^2=1.7$ for a least-squares analysis on only the fractional-order intensities and $\chi^2=1.8$ if both in-plane fractional- and integer-order data are refined. The latter gives $B_{\text{Cu}}=1.7\pm0.2$ Å^2 for the thermal Debye-Waller factor for the copper atoms in the missing-row layer, $B_{\text{O}}=0.0\pm0.4$ Å^2 for the oxygen atoms and a lateral displacement of 0.031 ± 0.005 Å of the copper atoms in the second layer towards the missing rows. Keeping in mind that the one-dimensional vibration amplitude is 0.083 Å, the displacement in the second layer is small but is necessary in order to obtain a good fit for the reflections with $h=\frac{5}{2}$. At the oxygen positions the electron-density plot in Fig. 1(b) has contours elongated along the (10) direction. Indeed, plotting the electron density with the structure factors calculated from our model gives identical shapes. Therefore, the elongation is an artifact resulting from a finite number of structure factors and cannot be attributed to an asymmetrical position of the oxygen atoms. By varying the oxygen position in the (1,0) direction we can conclude that the oxygen is located laterally in the copper rows to within 0.3 Å.

We now turn our attention to the out-of-plane atomic structure and focus on the crystal-truncation rods shown in Fig. 3. The scale factor is determined by the in-plane analysis, which now allows us to put the out-of-plane data on an absolute scale. In the limited-momentum-transfer range available in the direction normal to the surface, the CTR are not very sensitive to small relaxations in deeper layers and a three-parameter fit is sufficient. The result is that the copper atoms in the missing-row layer are relaxed outwards by 0.37 ± 0.05 Å relative to the positions for an ideally terminated surface, that the oxygen atoms are located 0.34 ± 0.17 Å below the first Cu layer, and finally that the second-layer atoms are insignificantly displaced by 0.0 ± 0.1 Å. The model gives $\chi^2=2.6$ and is shown as the full curve in Fig. 3. A model with the same parameters, but assuming the oxygen 0.34 Å *above* the first Cu layer, is shown as a dotted line and has $\chi^2=10.7$, and is not able to account for the data. Clearly, a much better determination could be achieved if data with larger momentum transfers normal to the surface were available. Deeper-layer relaxation with 2×1 symmetry will eventually be determined from fractional-order rod scans. It is worth noting that the model gives Cu—O bond lengths of 1.84 ± 0.17 and 1.81 ± 0.20 Å between the oxygen and the copper atoms in the missing-row layer and the second-layer atoms, respectively. These are close to the bulk value of 1.85 Å for Cu_2O.[13] The good agreement between the missing-row model, the CTR, and the in-plane integer-order reflections show that the surface is nearly 100% reconstructed.

In conclusion, by means of x-ray diffraction we have unambiguously shown that the Cu(110)2×1-O surface has a missing-row structure with oxygen atoms in long-bridge position placed 0.34±0.17 Å below the first copper layer. The structure is essentially the same as proposed by de Wit, Bronckers, and Fluit[3] and shows that the buckled-row model proposed on the basis of high-energy ion scattering[7] and later supported by STM (Ref. 8) was in error.

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