The structure of the oxygen-induced $c(6 \times 2)$ reconstruction of V(110)

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Abstract

The adsorption of 2.4 Langmuir oxygen on V(110) induces a $c(6 \times 2)$ reconstruction with an oxygen coverage of 0.5 ML. Its structure was determined using STM, quantitative LEED and ab initio density functional calculations in combination with molecular dynamics. Driven by the strong vanadium–oxygen bonding, the vanadium atoms at the surface are significantly rearranged compared to their bulk positions. The reconstructed geometry offers threefold and fourfold coordinated hollow sites, which are partially occupied by oxygen. The large set of structural data derived from LEED I–V analysis ($R_{Pe} = 0.11$) and ab initio calculations, as well as the experimental and simulated STM images agree well. Additionally the structure of clean V(110) was determined. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

At the beginning of structure analysis in surface science, the research was limited to simple structures, mostly clean metal surfaces, using quantitative low energy electron diffraction (LEED) for structure determination. With the development of the scanning tunneling microscope (STM) and the enhanced-computational power to perform reliable LEED and ab initio density functional theory calculations, the surface structures investigated and resolved became more complex. In this work we report on the determination of a surface structure significantly more complex than those of the early quantitative LEED studies, namely the oxygen-induced $c(6 \times 2)$ reconstruction. The combination of STM, quantitative LEED, ab initio density functional theory, finite temperature molecular dynamics (MD) simulations and Auger electron spectroscopy (AES) is a very powerful tool to investigate such a complex surface structure and achieve very reliable results. This work is part of a collaboration of both experimental and theoretical groups investigating the structure of
adsorbate covered vanadium single crystal surfaces. In previous works we determined the structure of the oxygen-induced \((1\times5)\) reconstruction of \(V(100)\) \cite{1} and the structures induced by carbon, where, depending on the additional amount of oxygen, \(p(1\times2)\) and \(c(2\times2)\) structures were observed \cite{2}. Additionally, the influence of the impurity carbon on a d-like surface state of \(V(100)\) was studied \cite{3}.

Adams and Nielsen \cite{4} first presented the structure of clean \(V(110)\) and reported the existence of the oxygen \(O-c(6\times2)\) phase on \(V(110)\). Although it is difficult to resolve the main oxygen Auger peak at 514 eV and the vanadium Auger peak at 509 eV, the oxygen coverage was estimated to be \(\approx 0.2\) ML. Kierren et al. \cite{5} studied the oxygen adsorption during epitaxial growth of \(V(110)\) on an \(\alpha\)-\(Al_2O_3\) surface confirming the oxygen coverage of 0.2 ML of the \(c(6\times2)\) reconstruction. Moreover they observed a \(p(11\times4)\) phase under special experimental conditions, for which a coverage of 0.13 \(\pm 0.02\) ML was proposed. However, according to the results of our study, the actual oxygen coverage of the \(c(6\times2)\) reconstruction is 0.5 ML.

Another work by Gourieux et al. \cite{6} investigated the influence of chemisorbed oxygen on the growth of Europium phases on \(V(110)\). Before the evaporation of Eu they observed the \(c(6\times2)\) superstructure induced by segregated oxygen. The corresponding STM image (which was not shown) was described as a kind of checkerboard on a mesoscopic scale.

2. Experimental and computational procedures

Two different ultra high vacuum (UHV) chambers were used for the STM and LEED measurements. The residual gas pressure was in the low \(10^{-11}\) mbar range in both chambers. An additional chamber was used in the STM system for sample preparation. All chambers are equipped with a sample manipulator allowing heating of the sample by electron bombardment. For the STM measurements we used a commercial room temperature STM (customized Omicron \(\mu\)-STM) with an electrochemically etched tungsten tip cleaned by sputtering.

AES (3 keV primary energy) with a cylindrical mirror analyzer was applied to determine the amount of impurities. In the case of the impurities carbon and oxygen, the total coverage can be estimated reliably using very recent results on \(V(100)\) \cite{1}. There we reported on the calibration of the carbon and oxygen Auger peaks on a \(V(100)\) surface with the Auger peak to peak height ratios of \(C_{272\,\text{eV}}/V_{473\,\text{eV}} = 0.16\) and \(O_{492\,\text{eV}}/V_{473\,\text{eV}} = 0.045\) for a coverage \(\Theta\) of 1 ML. Taking into account the different densities of atoms of \(V(110)\) compared to \(V(100)\), for \(V(110)\) we estimate the peak ratios of \(C_{272\,\text{eV}}/V_{473\,\text{eV}} = 0.22\) and \(O_{492\,\text{eV}}/V_{473\,\text{eV}} = 0.064\) corresponding to 1 ML in each case.

The LEED measurements were performed at room temperature at normal incidence of the primary electron beam. We used commercial two grid optics and video data acquisition. The earth’s magnetic field was shielded by more than 90\% through a \(\mu\)-metal chamber. The LEED images were recorded as eight bit images in steps of 1 eV and analyzed subsequently by image processing. The background subtracted \(I-V\) spectra were normalized to the current emitted by the electron gun, averaged over symmetry equivalent beams and smoothed in the Fourier domain. To improve the accuracy of the LEED \(I-V\) spectra of the faint superstructure spots of the \(c(6\times2)\) structure, we have used a procedure for image processing inspired by processing of astronomical CCD-images \cite{7}. From each LEED image the \textit{dark frame} image (no postacceleration of the electrons to the screen) was subtracted. The result was divided by the \textit{flat field} image (also \textit{dark frame} subtracted). The \textit{flat field} image was obtained as a LEED pattern of a polycrystalline area of the target holder. This procedure eliminates the effect of inhomogeneities of the LEED optics (grid, screen) and the CCD camera.

The LEED calculations were performed using the \textit{TensErLEED} program package \cite{8} which employs the Tensor LEED perturbation method \cite{9,10} to determine the structural and vibrational \cite{11} surface properties. The search for the best-fit structure was facilitated by an automated structural search procedure \cite{12}. The Pendry \textit{R}-Factor \cite{13} was chosen to measure the agreement between
the calculated and experimental $I-V$ spectra. The error bars of the best-fit structure were determined using Pendry’s variance, $\text{var}(R_{pe}) = R_{\text{min}} \sqrt{8V_0/\Delta E}$. For the clean V(110) surface the corresponding parameter was displaced and all other parameters were reoptimized within the Tensor LEED approximation, whereas for the reconstructed surface all other parameters were fixed at the best-fit values.

The ab initio calculations were performed by the Vienna ab initio simulation package (VASP) [14–16] applying ultrasoft pseudopotentials [17, 18]. A well-converged plane wave basis set was achieved by an energy cutoff of 500 eV. A generalized gradient approximation (GGA) to density functional theory [19] was utilized throughout this work. For bulk bcc vanadium a lattice constant of 2.99 Å was calculated being 1% smaller than the experimental value of 3.03 Å. The c(6 × 2) reconstructed surfaces were modelled by six layers of V within a repeated slab scheme with a vacuum corresponding to five layers. A $k$-point set corresponding to $4 \times 2 \times 1$ points for the full surface Brillouine zone was chosen. Tests with $6 \times 4 \times 1$ $k$-points indicate an accuracy better than 0.03 eV per adatom. The geometries were generally optimized until all forces were smaller than 0.03 eV/Å.

STM images were simulated from the ab initio VASP data following Tersoff and Hamann [20]. For constant current STM images, the local energy resolved density of states $\rho(r, \varepsilon_{\text{Fermi}})$ was evaluated and iso-surfaces of constant charge density $C = \rho(r, \varepsilon_{\text{Fermi}})$ were determined. The constant $C$ was chosen so that the core–iso-surface distance was larger than 2.6 Å.

The ab initio finite temperature MD were also performed with the VASP code on the Born Oppenheimer surface. The ionic equations of motions were integrated with a Verlet algorithm, and wave functions and the charge density were forward extrapolated between steps [15].

3. Cleaning of V(110)

AES measurements of the V(110) single crystal surface after polishing, sputtering in UHV for 2 h and annealing at 600 °C showed a contamination of the surface by carbon ($\Theta_C = 0.05$ ML), oxygen ($\Theta_O = 0.3$ ML) and sulphur ($S_{151 \text{ eV/}V_{473 \text{ eV}}} = 1.9\%$). The temperature dependent segregation behaviour of the main impurities (C, O, S) was similar to the V(100) single crystal surface [1]. In analogy to V(100), the impurities were removed by sputtering while repeatedly ramping the temperature between 150–600–400–600–150 °C. After a few days with this cleaning procedure we observed weak c(6 × 2) superstructure spots attributed to the presence of oxygen. Five hundred hours more of this cleaning procedure resulted in a removal of all impurities except carbon ($\Theta_C \approx 0.03$ ML). The corresponding diffraction pattern (Fig. 1, inset) has p(1 × 1) symmetry (no c(6 × 2) superstructure spots were visible).

4. Clean V(110)

The sputtered (500 eV Ar$^+$) and annealed (600 °C) V(110) single crystal exhibits p(1 × 1) symmetry. The carbon contamination of the V(110) single crystal after annealing was $\Theta_C \approx 0.03$ ML. The oxygen contamination was below the detection limit of our Auger spectrometer. Compared to
the results obtained on V(1 0 0) we can estimate the upper limit of the oxygen coverage to be $\Theta_O \approx 0.07$ ML. No other impurities were found with our Auger spectrometer. For the LEED $I$–$V$ analysis we used seven symmetry-in equivalent beams with a total energy range of $\Delta E = 1450$ eV. The first four interlayer distances and the vibrational amplitudes of the top and second vanadium layer were varied within the Tensor LEED approximation. The imaginary part of the inner potential, $V_\text{ib}$, was optimized full-dynamically. The real part was considered to be energy independent. The results of our LEED $I$–$V$ analysis ($R_{PU} = 0.108$) and ab initio calculations are shown in Table 1 together with the results obtained by Adams and Nielsen [4] 20 years ago.

All three analysis found a contraction of the first layer distance. Compared to the LEED study of Adams and Nielsen (−1%), the contraction is even larger in our recent LEED (−3.3%) and VASP study (−5%). The rather small discrepancy may be due to the presence of carbon and, possibly, oxygen. Although the amount is small ($\Theta_C \approx 0.03$ ML) it might be sufficient to reduce the contraction compared to a perfectly clean V(1 1 0) surface. Moreover, the influence of density functional approaches on the calculated layer spacings has been investigated extensively in a previous paper on V(1 0 0) [2] for which the surface layer relaxation is much more pronounced. The vibrational amplitudes of the first and second vanadium layer were determined by LEED to $\text{vib}_1 = 0.18 \pm 0.02$ Å and $\text{vib}_2 = 0.14 \pm 0.015$ Å, respectively. The vibrational amplitudes for the deeper layers were fixed at the bulk value of $\text{vib}_b = 0.133$ Å. For the inner potential we found $V_{\text{ib}} = 6.5$ eV and $V_b = 5.3$ eV as the best-fit values.

5. c(6 × 2) reconstruction

5.1. Preparation of the c(6 × 2) reconstruction

We have dosed oxygen at 250 °C sample temperature on the sputtered (500 eV Ar$^+$) and annealed (600 °C) V(1 1 0) single crystal. After gas exposure to a dose of 2.4 Langmuir (1 Langmuir = 1L = 1.33 × 10$^{-6}$ mbars), the diffraction pattern reveals sharp c(6 × 2) superstructure spots of two coexisting mirror-image domains (Fig. 1). The total oxygen coverage of the reconstructed surface can be estimated by AES as $\Theta_O \approx 0.6$ ML. Taking into account the c(6 × 2) symmetry, models with $\Theta_O = 0.66$ ML and $\Theta_O = 0.5$ ML should be considered in the LEED and ab initio calculations for the structure determination.

5.2. Scanning tunneling microscopy

Fig. 2a shows an STM image of the c(6 × 2) reconstructed V(1 1 0) surface. The primitive (rectangular) unit cells of the c(6 × 2) superstructure are drawn in the left bottom corner. Two mirror-image domains are clearly visible in this STM image (indicated by the dark lines running along the [1 1 2] and [1 1 2] directions). The different domains are separated by brighter areas. These areas are not islands (the apparent height difference to the maxima of the ordered areas is only 10–20 pm). Fig. 2b shows the same surface with higher resolution. However, even now the vanadium atoms are not resolved. Instead, one observes an elongated bright spot in the center of each c(6 × 2) unit cell (frame b).

In the experimental STM images, the short side of the unit cell appears brighter, whereas the long side of the unit cell clearly shows two black spots. From these STM images alone we cannot derive the structure of this reconstruction, but three things help to get an idea about the actual structure: first, comparing this structure with the

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LEED (this work)</th>
<th>LEED [4]</th>
<th>VASP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{12}$ (Å)</td>
<td>$2.07 \pm 0.02$</td>
<td>$2.12 \pm 0.02$</td>
<td>$2.01$</td>
</tr>
<tr>
<td>($-3.3%$)</td>
<td>($-1%$)</td>
<td>($-5%$)</td>
<td></td>
</tr>
<tr>
<td>$d_{23}$ (Å)</td>
<td>$2.14 \pm 0.02$</td>
<td>$2.14$ (fix)</td>
<td>$2.09$</td>
</tr>
<tr>
<td>$d_{34}$ (Å)</td>
<td>$2.13 \pm 0.025$</td>
<td>$2.14$ (fix)</td>
<td>$2.11$</td>
</tr>
<tr>
<td>$d_{60}$ (Å)</td>
<td>$2.13 \pm 0.04$</td>
<td>$2.14$ (fix)</td>
<td>$-$</td>
</tr>
<tr>
<td>$d_{\text{bulk}}$ (Å)</td>
<td>$2.14$ (fix)</td>
<td>$2.14$ (fix)</td>
<td>$2.11$ (fix)</td>
</tr>
<tr>
<td>$V_{\text{ib}}$ (eV)</td>
<td>$6.5$</td>
<td>$8.4 \pm 1.5$</td>
<td>$-$</td>
</tr>
<tr>
<td>$V_b$ (eV)</td>
<td>$5.3$</td>
<td>$6.6 \pm 0.6$</td>
<td>$-$</td>
</tr>
</tbody>
</table>

Description of columns see text.
oxygen-induced (1 x 5) reconstruction of V(110), one may suppose that unoccupied adsorption sites are imaged as bright spots, whereas occupied adsorption sites are black. This means that the elongated bright spots in the center of the unit cell are attributed to unoccupied adsorption sites, whereas at the sides of the rectangular unit cell oxygen should be present. Second, another hint for solving this complex structure is given by the STM image shown in Fig. 2c. There the amount of dosed oxygen was less than in the previous cases. The result was that the long range order was less developed and some areas with two translational domains could be found. Fig. 2c shows a domain boundary, where the initially elongated bright spots are now split up into two spots. This indicates that the center of the c(6 x 2) unit cell is oxygen-free, since it would be energetically unfavourable to have such a high number of neighbouring oxygens as it would be in a domain boundary formed by occupied adsorption sites. Third, in situ STM measurements showed no changes of the size and shape of the terraces during oxygen adsorption and the step edges remain straight. This means that no mass transport of the vanadium atoms is involved in the formation of the c(6 x 2) reconstruction. We conclude that the c(6 x 2) unit cell consists of the same number of V atoms as the corresponding area of the unreconstructed surface, i.e., 6 V atoms per layer.

The STM images and the AES data fortunately restrict the amount of possible structure models. The oxygen coverage should be 0.5 or 0.66 ML with six vanadium atoms per unit cell and the symmetry of each unit cell should correspond to the STM images.

5.3. Structure determination by trial and error

Fig. 3a shows a bulk like bcc(110) surface. The size of the c(6 x 2) cell (parallelogram) and the corresponding primitive cell (rectangle) is drawn. This unreconstructed surface provides no favourable adsorption sites like symmetric threefold or fourfold hollow sites. We therefore expect a rearrangement of the vanadium atoms (at least) in the first layer. One possible lateral rearrangement of the initially close-packed bcc(110) surface is shown in Fig. 3b. Compared to model Fig. 3a one row of vanadium atoms is shifted up (r1) and one row is shifted down (r2). The resulting surface could be viewed as consisting of 3-atom wide stripes of a close-packed structure. The recon-
structed surface layer now has threefold and fourfold coordinated hollow sites.

The first model which was calculated (Fig. 3b) has an oxygen coverage of $\Theta_O = 0.66$ ML. Every fourfold hollow site is occupied by oxygen. The threefold hollow sites are occupied in the way that all oxygen atoms form a rectangular pattern. This model is compatible with the symmetry observed in the STM images. In the center of the unit cell there are unoccupied hollow sites, which should be imaged as bright spots, and the occupied adsorption sites should appear as depressions in the STM images. Ab initio calculations found an adsorption energy of $-5.10$ eV per oxygen atom. The LEED analysis resulted in a Pendry $R$-factor of $R_{Pe} = 0.17$. Usually, an $R$-factor of $R_{Pe} = 0.17$ for an adsorbate covered surface can be considered to be quite good, and the structure can be considered to be solved. But two points lead to the exclusion of this model to be the correct one: first, the distances between the oxygen atoms in threefold and fourfold hollow sites are very small ($\approx 2.2$ Å). The repulsive O–O interaction is not sufficiently screened by the metal over such a short distance, resulting in a less favorable adsorption energy compared to structural models with larger O–O distances at the same O coverage (see next paragraph). Second, the simulated STM image does not agree with the experimental one. Nevertheless, due to the good Pendry $R$-factor the correct structure of the c(6×2) reconstruction should not differ significantly from model Fig. 3b.

The next considered model for $\Theta_O = 0.66$ ML is shown by Fig. 3c. The arrangement of the vanadium atoms in the first layer is the same as in model Fig. 3b. Again, every fourfold hollow site is occupied by oxygen. The only difference is that the occupied threefold hollow sites changed, forming a zig-zag pattern. As derived from the ab initio calculations, this model is more stable by 0.25 eV per oxygen atom compared to Fig. 3b, but the Pendry $R$-factor is now 0.35, twice as large as in the previous case. Moreover, the symmetry of the unit cell in the STM images is not reproduced. Finally, simulated STM images of this model do not agree with the experimentally observed one, excluding this model as the correct structure model.

Removing one oxygen atom from one fourfold hollow site in Fig. 3b results in an oxygen coverage of $\Theta_O = 0.5$ ML (Fig. 3d). This model has the symmetry observed in STM with reasonable O–O distances. The ab initio calculations yielded an adsorption energy of $-5.10$ eV (the largest oxygen binding energy among these models) and the simulated STM image is in agreement with the experimental one (see below). The Pendry $R$-factor is lowered to 0.11. Since an even lower $R$-factor is hardly to be expected and this model is compatible with all results presented so far, it is the best candidate for the experimentally observed oxygen-induced c(6×2) reconstruction of V(110).

Since we know from our previous paper [1] that it is difficult to estimate the correct oxygen coverage, we even tried a model with a higher coverage of 83% and the proper symmetry. In this model, all threefold hollow sites were occupied by oxygen, but only every second fourfold hollow site. With that high coverage of oxygen, it was difficult to obtain convergence in our calculations. When we finally succeeded, the small adsorption energy showed that this model is physically irrelevant. Also the calculated $R_{Pe}$ of more than 0.6 excluded this model.

5.4. Finite temperature molecular dynamics

Although the agreement between experiment and theory was very good at this stage, we decided to seek for an additional confirmation of the structure shown in Fig. 3d. Until this point, the calculations were strongly biased by the experimental results, in particular by the observed STM images. But certainly it should be possible to calculate the energy of all conceivable structures with c(6×2) symmetry, and to seek the one with the lowest energy. This structure should correspond to the model determined in the previous section. To perform this exhaustive search of the phase space we have utilized a simulated annealing approach based on ab initio finite temperature MD [15]. Three such MD simulations were performed, two with three oxygen atoms adsorbed on a c(6×2) slab and one with four oxygen atoms. To make the calculations computationally less demanding, compromises between accuracy and calculational
speed had to be made. First, the number of layers was reduced from six to four, and only the two topmost layers were allowed to move. Second, a single $k$-point with the coordinate $(1/4,1/4,0)$ was used for the MD simulations, and finally, a softer oxygen potential requiring only an energy cutoff of 250 eV was applied. This reduces the computational requirements by roughly one order of magnitude, but introduces errors of the order of 50 meV; certainly a reasonable compromise, considering that it is now possible to perform a significantly more exhaustive search of the phase space.

As starting geometries, the undistorted ideal c$(6 \times 2)$ supercell was used, and three and four oxygen atoms, respectively, were placed on the surface (cf. Fig. 4a). Next the system was heated to 2000 K and equilibrated for roughly 5 ps, then the temperature was gradually reduced to 800 K in another 5 ps. For the simulation with three oxygen atoms, several snapshots of the positions evolving during the MD simulation are shown in Fig. 4. The initial configuration is rapidly destroyed, and after 5 ps, the substrate has rearranged so that all oxygen atoms can find threefold hollow sides (Fig. 4e). Upon cooling, the substrate and the oxygen atoms rapidly adopt a similar geometry as shown in Fig. 3d. After the final annealed structure was quenched into the next local minimum and after the $k$-point density was increased to the previous setup, an identical structure as in the previous section was obtained. To be sure that the simulation had not been trapped in a local energy minimum, the simulated annealing run was repeated starting from a different initial geometry, but the final structure was again identical to Fig. 3d. Next, a simulation with four oxygen atoms in a c$(6 \times 2)$ supercell was performed. In this case, the structure shown in Fig. 3c was obtained.

In summary, the finite temperature MD fully confirm the results of the previous section. They show that the structures indicated in Fig. 3c and d are not only local energy minima but global ones, if four and three oxygen atoms per unit cell, respectively, are adsorbed on the V(1 1 0) surface.

5.5. Structural details

For the final structure determination by LEED we varied 33 independent parameters: the vertical displacements of the oxygen overlayer and the topmost three vanadium layers. In plane displacements were considered for the oxygen adlayer and the topmost two vanadium layers. Additionally, the vibrational amplitudes of the oxygen overlayer and two vanadium layers were optimized within the Tensor LEED approximation. The real and imaginary part of the inner potential ($V_{0r}$ and $V_{0i}$) were optimized full dynamically with the best-fit values of $V_{0r} = 8$ eV and $V_{0i} = 4.5$ eV. The energy overlap was $\Delta E = 3670$ eV resulting in a variance of $\text{var}(R_{\text{PE}}) = 0.01$. The excellent agreement of the calculated and experimental $I-V$ spectra is shown in Fig. 5. The structure determined by LEED and ab initio calculations is summarized in Table 2. The naming of the atoms is according to Fig. 6. The first digit of the index denotes the layer, the second the atom number within the unit cell. In the third layer the atom V$_{3i}$ is the atom below V$_{1i}$ before the shift in the surface occurs (ABAB stacking).

In case of the vanadium atoms V$_{ij}$, $\Delta x$ and $\Delta y$ correspond to the displacement relative to the bulk-like positions. In case of O$_i$, $\Delta x$ and $\Delta y$ are relative to the origin of the Cartesian coordinate system, i.e., the position of V$_{11}$ (Fig. 6). $\Delta z$ is the deviation from the center of mass of the corresponding layer, where positive $z$ points to the vacuum. For the oxygen atoms, $\Delta z$ is the distance to the averaged first vanadium layer. In the LEED as well as in the VASP calculation, each vanadium
layer consists of only four independent atoms due to the p2 symmetry. For two atoms per layer, in-plane displacements are not allowed (denoted by (f) in Table 2).

Comparing now the LEED and VASP results, we find generally excellent agreement, with the exception of the height of the oxygen atom O₃ (see below). In the following, we give the corresponding group of numbers in the form (LEED, VASP). Compared to the clean surface, the inward relaxation of the first vanadium layer is lifted now. \( d_{12} \) is close to the bulk value (2.13, 2.11) Å. Also the deeper interlayer distances have no significant deviation from the bulk value. The oxygen atoms in threefold hollow sites stay \( \approx 1.1 \) Å above the first vanadium layer. The oxygen atom in fourfold hollow site, O₃, resides (0.32, 0.74) Å above the vanadium layer. We found a large buckling of the vanadium atoms in the first layer. The vanadium atom V₁₁, which has two oxygen atoms as neighbours is (0.16, 0.17) Å above the center of mass of the first layer. Atom V₁₂, however, which has no

Fig. 5. Comparison between experimental (black) and calculated (gray) LEED \( I-V \) spectra of the best-fit model Fig. 6. The energy overlap is 3570 eV. The Pendry R-factor is 0.11.
ab initio calculations. Fig. 6. The best-fit structural model of the oxygen-induced c(6 × 2) reconstruction on V(110) determined by LEED and ab initio calculations.

<table>
<thead>
<tr>
<th>Atom</th>
<th>LEED</th>
<th>VASP</th>
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<tbody>
<tr>
<td></td>
<td>Δx (Å)</td>
<td>Δy (Å)</td>
</tr>
<tr>
<td>O1,2</td>
<td>1.64 ± 0.09</td>
<td>−0.08 ± 0.12</td>
</tr>
<tr>
<td>O3</td>
<td>3.71 (f)</td>
<td>2.62 (f)</td>
</tr>
<tr>
<td>V11</td>
<td>0 (f)</td>
<td>0 (f)</td>
</tr>
<tr>
<td>V12</td>
<td>0 (f)</td>
<td>0 (f)</td>
</tr>
<tr>
<td>V13,14</td>
<td>0.01 ± 0.05</td>
<td>0.28 ± 0.06</td>
</tr>
<tr>
<td>V15,16</td>
<td>−0.19 ± 0.05</td>
<td>0.32 ± 0.05</td>
</tr>
</tbody>
</table>

| Δd12 (Å) | −0.5% | 0.0% |
| Δd26 (Å) | −0.9% | −0.2% |
| Δd34 (Å) | −0.3% | −0.9% |

The naming of the atoms is according to Fig. 6. f means that the corresponding atom was fixed to the bulk-like position due to symmetry, nv means that the parameter was not varied.

Table 2: Comparison of the geometry of the oxygen-induced c(6 × 2) reconstruction on V(110) determined by LEED and ab initio calculations.

Fig. 6. The best-fit structural model of the oxygen-induced c(6 × 2) reconstruction of V(110) determined by LEED and ab initio calculations.

oxygen neighbour, is the deepest one in the first layer (−0.22, −0.30)Å. The remaining atoms have nearly the same height and just small deviations from the average level. The in-plane displacements of the vanadium atoms are very large. The deviation from the bulk-like positions \( \Delta r = \sqrt{(\Delta x)^2 + (\Delta y)^2} \) is (0.28, 0.31)Å for atom V13 and (0.37, 0.30)Å for atom V15. In the second vanadium layer the buckling is smaller. Atom V23, which has no oxygen above, is shifted outwards remarkably (0.09, 0.12)Å. The in-plane displacements are also less pronounced. The deviation compared to the bulk-like positions is maximum 0.04 Å.

For the vibrational amplitudes derived from the LEED calculations, we found a high value of 0.25 Å for O3, a value 0.19 Å for O1 and O2. The amplitudes of the atoms V11 are in the range between 0.16 and 0.19 Å. In the second layer all amplitudes were considered equal resulting in the best-fit value of 0.15 Å, comparable to the vibrational amplitudes in the bulk (0.13 Å).

In view of the different O3 height and the difference of the STM images (see below), tests were made to exclude effects of how the bulk continuation is simulated in the ab initio calculations. We have tried two methods. First, the bottom side of
the slab was fixed at the bulk terminated geometry. In the second calculation, we started with the clean surface, where all six layers were allowed to relax. Then the vanadium atoms in the first layer were shifted, the oxygen atoms added, and the adsorbates and first three vanadium layers were allowed to relax. Our test calculations, however, indicate that differences in the bulk continuation have no significant effect on the final structure and relative energies.

5.6. Simulated STM image

We now turn to Fig. 7, which is used for the interpretation of the experimental STM images. The structure of the best-fit model (bottom) is presented together with the experimental STM image, the STM image simulated using the LEED best-fit geometry, and the STM image simulated using the relaxed geometry as determined by VASP. Quite good agreement is found. The elongated bright spot in the center of the unit cell corresponds to the unoccupied threefold hollow sites. This is in analogy to the O-(1 × 5) system, where unoccupied fourfold hollow sites appear as bright spots [1]. The dark spots are attributed to the presence of electronegative oxygen atoms in the threefold hollow sites.

In the experimental STM image, the short side of the unit cell, where the oxygen atoms are located in fourfold hollow sites, appears to be brighter than the occupied threefold hollow site. In the simulated STM image utilising the VASP geometry it is the other way round, i.e., the short side of the unit cell is darker than the long side. This discrepancy between the simulated and experimental STM image at the oxygen in the fourfold hollow site (denoted as O3 in Table 2) may be attributed to the fact that in the ab initio simulation, O3 is higher above the surface by 0.42 Å than in the LEED best-fit structure, obviously leading to darker spots in the image. This difference also leads to a larger lateral distance between the two black spots on the longer side of the cell. To exclude that these deviations are an artefact of the Tersoff Hamann approach, we simulated an STM image using the LEED best-fit geometry. This yields an STM image in perfect agreement with experiment. Therefore, the main discrepancy between experimental and theoretical STM image is related to the difference in height of the fourfold coordinated oxygen atom.

For O3, the ab initio calculations show a very unusual, nearly flat energy minimum for 0.68 <
suggesting large vibrational effects. The LEED height of this oxygen atom is 0.32 \text{ Å} (Table 2), which is even closer to the surface. However, this best-fit LEED geometry does not result in an energy minimum in the VASP calculations. The VASP optimized model (with its larger O3 distance) is more stable by about 0.1 eV. On the other hand, LEED calculations with $z = 0.80$ and 0.68 Å resulted in an Pendry $R$-factor of $R_{Pe} = 0.19$ and 0.17, respectively. The $R$-factor is lowered monotonously, when $z$ moves to the best-fit value of 0.32 Å. To exclude technical problems in our calculations, we increased the $k$ point set to $(6 \times 4 \times 1)$, and used different cells (relaxed and bulk terminated) as described in Section 5.5. But in all the cases the structural results were the same.

Further calculations were also made by replacing the oxygen atom in the fourfold hollow site, O3, by carbon (cf. Fig. 6). In this case, the C atom is located 0.34 Å above the V surface which would agree very well with the mentioned LEED best-fit geometry (only oxygen). The calculated STM image (now with carbon), however, did not change significantly. Based on these ab initio calculations, additional LEED calculations were performed. First, O3 was also replaced by carbon and second, O3 was replaced by a mixture of oxygen and carbon within the average t-matrix approximation [21]. The latter case was additionally split up in two search procedures: first, the height of the oxygen and carbon in the fourfold hollow site was set to the same value and second, different heights were considered. The differences in the Pendry $R$-factor of all three calculations are less than 0.001, indicating the low sensitivity to this parameter. In the case of pure carbon in the fourfold hollow site, the height of this atom above the first vanadium layer is lowered by 0.2 Å in comparison with the corresponding oxygen atom to 0.12 Å. The discrepancy between the LEED and VASP results is therefore somewhat decreasing from 0.42 Å in the oxygen case to 0.22 Å in the carbon case. From the LEED result the exact determination of the occupied species is rather uncertain, but the AES result ($\Theta_C = 0.03$ ML) excludes all configurations except an occupation with almost 100% oxygen.

6. Discussion

With STM, quantitative LEED, and ab initio density functional theory we have determined the structure of the oxygen-induced c(6 × 2) reconstruction of V(110). We found large in-plane displacements of the first vanadium layer which provide roughly threefold and fourfold coordinated hollow sites. These adsorption sites are partially occupied by oxygen, resulting in a total coverage of $\Theta_O = 0.5$ ML (see Fig. 6). The global stability of the suggested structure was confirmed by finite temperature MD.

Given the complexity of the structure, we found a good overall agreement of the geometry determined by LEED and ab initio calculations. The contraction of the first interlayer distance of the clean surface is lifted by oxygen. Moreover, all deviations relative to the bulk are in good agreement for both methods. A strong buckling of the first vanadium layer is found in LEED and ab initio calculations. The vanadium atom V12, which has no oxygen as a neighbour, is the deepest one, whereas the atom V11, which is surrounded by two oxygen atoms is shifted significantly upwards. This trend reflects the usual dependence of relaxation on adsorbate coverage. The oxygen atoms in the threefold hollow sites are highest, and the oxygen atoms in fourfold hollow sites are closer to the surface. However, the absolute value of the position of the latter atom (O3) is different in LEED ($D_z = 0.32$ Å) and theory ($D_z = 0.74$ Å). The comparison with the calculated STM images indicates that the actual structure is close to the LEED result.

The vanadium–oxygen bond lengths shown in Table 3 point at a likely reason for the discrepancy. The theoretical V–O bonds are approximately 1–2% longer than the experimental ones. Similar overestimations of the bond lengths are found for bulk vanadium oxides [22]. We also remind the reader that the theoretical V–V bond length is underestimated by more than 1% in bcc V. This combination could yield a too elevated position for the fourfold coordinated oxygen atom in our ab initio calculations. To test this hypothesis, we increased the lateral lattice constant of the V slab modestly by 1.5%, and relaxed the top three
V layers and the oxygen atoms again. Now the position of the fourfold O atom was in almost perfect agreement with experiment ($D_z = 0.37 \text{ Å}$). The position of the threefold coordinated O atoms remained essentially unchanged ($D_z = 1.13 \text{ Å}$). In summary, we conclude that the agreement of the structural data of experiment and ab initio calculations is very good for this rather complex case. The notable discrepancy for the fourfold coordinated oxygen atom is most likely related to a slight overestimation of the oxygen–vanadium and underestimation of the vanadium–vanadium bond lengths in the GGA calculations.

The remaining question is the driving force behind this reconstruction. This can be answered following the arguments of the O-(1×5)/V(100) paper [1]: the vanadium–oxygen bond lengths of some vanadium oxides (VO, VO$_2$, V$_2$O$_3$ and V$_2$O$_5$) reveal that the bond lengths are in the range between 1.88 and 2.04 Å, except the small double bond in V$_2$O$_5$ of 1.58 Å (Table 2 in Ref. [1] or [23]). For O-(1×5)/V(100) the preferred bond length seems to be 1.9 Å. We therefore also expect vanadium–oxygen bond lengths of ≈1.9 Å for c(6×2)/V(110).

Let us assume an oxygen occupation on the asymmetric fourfold hollow sites of the unreconstructed V(110) surface (Fig. 3a). If the average bond length between the oxygen atom and the two vanadium atoms $V_1$ and $V_2$ were 1.9 Å (see Fig. 3a), then the height of the oxygen atom had to be 0.58 Å above the first vanadium layer. This would result in oxygen–vanadium bond lengths of 2.22 Å (O–$V_1$), 1.62 Å (O–$V_2$) and 2.72 Å to the vanadium atom in the second layer. The large spread of the bond length is certainly not favourable. Therefore, if oxygen adsorbs on the clean V(110) surface, the oxygen atoms induce a strong stress on the vanadium substrate, since the bulk-like surface does not offer favourable adsorption sites. This stress is released by large displacements of the vanadium atoms in the first layer resulting in a geometry of the top vanadium layer where the oxygen atoms can be bound to more vanadium atoms with comparable bond lengths. Therefore we think that the main reason for the c(6×2) reconstruction is the optimization of the vanadium–oxygen bond lengths. Table 3 shows the oxygen–vanadium bond lengths determined by LEED and ab initio calculations (VASP), which agree well. The average bond length including the threefold coordinated oxygen atom $O_1$ (1.85, 1.88) Å is a little bit smaller than the average bond length for the fourfold coordinated oxygen atom $O_3$ (1.92, 1.95) Å. This reflects the usual increase of bond lengths with increasing coordination. The difference of the bond lengths of an oxygen atom to the individual vanadium atoms is less than 0.05 Å. This scenario is also confirmed in the finite temperature MD, where the substrate changed in the first few ps in such a way that all oxygen atoms have three neighbours. Upon cooling the final structure is obtained.

Interestingly the ab initio calculations reveal that these arguments are also valid for the purely hypothetical structures calculated for higher coverage: the substrate again reconstructs, and now all fourfold coordinated sites are occupied (Fig. 3c). The ab initio calculations indicate that the additional fourth oxygen atom has an adsorption energy of $E_{ads} = 3.8 \text{ eV}$. These calculations also show that repulsion between oxygen atoms separated by less than one vanadium–vanadium distance is an important factor for determining the structure.

7. Summary

The adsorption of 2.4 L oxygen at 250 °C induces a c(6×2) reconstruction of the V(110)
single crystal surface. Using three different methods (STM, quantitative LEED and ab initio density functional theory) we determined the structure of this unusual reconstruction. Driven by the strong vanadium–oxygen bond the vanadium lattice of the first layer is distorted significantly providing threefold and fourfold hollow sites for oxygen adsorption. These adsorption sites are filled partially (coverage $\theta_0 = 0.5$ ML) leading to the experimentally observed rectangular pattern. Compared to the clean surface, where we found a contraction of the first interlayer distance, the inward relaxation is lifted. The preferred vanadium–oxygen bond length is $\approx 1.9$ Å as determined by both the LEED and the ab initio calculations.

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