

Oxygen adsorption on the Ru ($10\bar{1}0$) surface: Anomalous coverage dependence

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Oxygen adsorption onto Ru ($10\bar{1}0$) results in the formation of two ordered overlayers, *i. e.* a $c(2\times 4)$ -2O and a (2×1) pg-2O phase, which were analyzed by low-energy electron diffraction (LEED) and density functional theory (DFT) calculation. In addition, the vibrational properties of these overlayers were studied by high-resolution electron loss spectroscopy. In both phases, oxygen occupies the threefold coordinated hcp site along the densely packed rows on an otherwise unreconstructed surface, *i. e.* the O atoms are attached to two atoms in the first Ru layer Ru(1) and to one Ru atom in the second layer Ru(2), forming zigzag chains along the troughs. While in the low-coverage $c(2\times 4)$ -O phase, the bond lengths of O to Ru(1) and Ru(2) are 2.08 Å and 2.03 Å, respectively, corresponding bond lengths in the high-coverage (2×1) -2O phase are 2.01 Å and 2.04 Å (LEED). Although the adsorption energy decreases by 220 meV with O coverage (DFT calculations), we observe experimentally a shortening of the Ru(1)-O bond length with O coverage. This effect could not be reconciled with the present DFT-GGA calculations. The $\nu(\text{Ru-O})$ stretch mode is found at 67 meV [$c(2\times 4)$ -2O] and 64 meV [(2×1) pg-2O].

I. INTRODUCTION

The actual adsorption geometry of atoms and molecules at metal surfaces, *i. e.* the adsorption site and the bond lengths of an adsorbate to its attached substrate atoms, is essentially the result of a delicate balance between reaching the optimum surface charge density by the adsorbate, minimizing the Pauli repulsion between occupied orbitals of the adsorbate and the metal surface, and optimizing the electrostatic interaction between the adspecies [1]. If the charge density at the surface is modified, for example, due to coadsorbed atoms or molecules, the adsorption geometry of the pre-adsorbed species on the surface can vary widely. Illustrative examples have only recently been reported in the literature in that adsorption sites have shown to switch upon coadsorption [2]. Not only in heterogeneous (*i. e.* coadsorption) systems but also in homogeneous systems (*i. e.* for a single adsorbate) the adsorption geometry might change upon varying the density of adparticles since both the effective charge density at the surface and the adsorbate-adsorbate interaction change appreciably. Notable variations in the adsorption geometry of such homogeneous systems have been reported for alkali metal adsorption: For instance, with increasing coverage the adsorption site shifted either from on-top to hcp sites, as for the case of Cs on Ru (0001) [3a], or the coordination of adsorption was preserved, but still the adsorption site changed from fcc to hcp, as encountered with the system K/Ru (0001) [3b]. Similar effects were identified with DFT calculations for alkali metal adsorption on the (111) and (100) surfaces

of Al [4].

With oxygen adsorption a change in adsorption site with coverage has not been identified so far, although for the O/Co ($10\bar{1}0$) system such a change was proposed on the basis of recent scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) investigations [5]. On Co ($10\bar{1}0$) oxygen forms a low-coverage $c(2\times 4)$ -2O phase, which upon heating transforms irreversibly into a (2×1) -1O phase, and a high-coverage (2×1) -2O phase [6]. There is, however, only scant evidence for O atoms changing their adsorption site from fcc to hcp when going from the $c(2\times 4)$ -2O to the (2×1) -1O overlayer; threefold coordinated fcc and hcp sites are characterized by one and two substrate atoms in the topmost layer, respectively. While the chemisorption of oxygen into hcp sites in the (2×1) pg-2O phase has been recently confirmed with LEED [7], the fcc adsorption site of $c(2\times 4)$ -2O still remains speculative, as it is only concluded from the high intensity of the LEED superstructure spots, which was interpreted in terms of strong lateral distortions of the substrate atoms [5]. On the Ru ($10\bar{1}0$) surface, which is much easier to prepare and to clean than Co ($10\bar{1}0$), oxygen adsorption also leads to the formation of $c(2\times 4)$ -2O and (2×1) pg-2O overlayers [8]. However, the low O coverage phase on Ru ($10\bar{1}0$) is the thermodynamically stable one, while on Co ($10\bar{1}0$) the $c(2\times 4)$ -2O phase serves just as a precursor state for the stable (but heavily reconstructed [9]) (2×1) -1O surface. Neither the clean Ru ($10\bar{1}0$) nor the oxygen-covered surfaces have been subjected to a LEED analysis so far. The motivation for the project discussed in this paper

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was to learn about the interaction of oxygen with the underlying Ru(10 $\bar{1}$ 0) surface and about the modification of the local bonding configuration upon increasing the O coverage. For this purpose, we applied LEED for the determination of the atomic geometries, high resolution electron loss spectroscopy (HREELS) for examining the vibrational properties, and density functional theory (DFT) calculations to determine the energetics at this surface.

II. EXPERIMENTAL AND CALCULATIONAL DETAILS

A. HREELS

The HREELS measurements were performed in a second UHV apparatus with a base pressure of 2×10^{-11} mbar. The apparatus consisted of two chambers. The upper chamber contained an argon ion gun, a quadrupole mass spectrometer, and a LEED optics. The lower chamber housed a HREELS spectrometer for recording the vibrational spectra, capable of an energy resolution of $\Delta E = 1$ meV in the reflected beam, was used at $\Delta E = 1.9$ meV across the sample with typical count rates of 3×10^5 counts per second in the elastic peak. The HREEL spectra were all taken at a 60° angle of incidence with respect to the surface normal and in specular geometry; the sample temperature was 293 K. The energy resolution was set to be 1.9 meV. In order to allow for direct comparison of HREELS and LEED results, the same sample and the same cleaning protocol were used.

B. LEED

The LEED experiments were conducted in an ultrahigh-vacuum chamber (with base pressure 2×10^{-10} mbar) equipped with a four-grid LEED optics, Auger electron spectroscopy (AES) and facilities for surface cleaning and characterization. The LEED intensity data were recorded at 110 K using a video-LEED system [10]. The recorded LEED data were fed into a full-dynamical LEED program developed by Moritz [11] which is also equipped with a least-squares optimization scheme [12] in order to perform the simultaneous and automated refinement of structural (as well as non-structural) parameters. The degree of agreement between calculated and experimental data was judged by the reliability factors R_P [13] and R_{de} [14] which were also the quantities to be minimized in the optimization scheme. The scattering from Ru and O was treated by using up to nine phase shifts which were corrected for thermal vibrations by employing Debye temperatures of 420 K for Ru and 450 K for O. These temperatures were not refined. The phase shifts have already been

used in a previous LEED analysis of the (1 \times 1)-O surface structures of Ru(0001) [15]. The LEED analysis was carried out in two steps. First, an exhaustive grid search over a wide range in parameter space was conducted for both O phases with the unrelaxed substrate and the oxygen-ruthenium interlayer spacing being the only structural parameter. In the next step, starting from the optimum parameter values found by the grid searches, automated structure refinements were carried out. Apart from the first three layer spacings, lateral and vertical displacements of Ru atoms in the first and second layer (preserving the corresponding local symmetry of the adsorbate) were simultaneously and automatically refined.

In both chambers (HREELS and LEED), the Ru(10 $\bar{1}$ 0) sample was cleaned by argon ion bombardment at 1 keV followed by cycles of oxygen adsorption and thermal desorption in order to remove surface carbon. Final traces of oxygen were removed by flashing the surface to 1530 K, resulting in a sharp (1 \times 1) LEED pattern (cf. Fig. 1) and no impurity losses in HREELS. The phases of c(2 \times 4)-2O and (2 \times 1)-2O were prepared by exposing the clean Ru(10 $\bar{1}$ 0) at room temperature to 0.7 L and 2.5 L oxygen, respectively, (cf. Fig. 1). From AES measurements, the ratio of global oxygen coverages in the two ordered overlayers was 1 : 2. Together with the observation of a glide plane symmetry in the (2 \times 1) phase, one can safely assume that both c(2 \times 4) and (2 \times 1) structures contain two O atoms in the unit cell. At room temperature, the (2 \times 1) LEED pattern exhibits a glide symmetry plane along the [1 $\bar{2}$ 10] direction, as inferred from the missing fractional-order spots $(n+1/2, 0)$, $n = 0, \pm 1, \dots$ at normal electron incidence; the proper nomenclature for this oxygen phase is therefore (2 \times 1)pg-2O.

Exposing a (2 \times 1)pg-2O structure to NO $_2$ at 500 K sample temperature, we tried to prepare an ordered O overlayer structure with coverage exceeding 1 ML. The same procedure has already been used successfully for the formation of the (1 \times 1)-O structure on Ru(0001) [15]. On Ru(10 $\bar{1}$ 0), however, this procedure leads only to a streaky (1 \times 2) phase in a wide O coverage range from 1.2 ML to 3...4 ML as estimated from AES and TDS measurements. Obviously, a (1 \times 1)-2O is not the most stable configuration at Ru(10 $\bar{1}$ 0) under these experimental conditions, but it may exist as a metastable phase (cf. the DFT calculations below).

C. DFT calculations

The density functional theory (DFT) calculations were performed using the generalized gradient approximation (GGA) of Perdew et al. [16] for the exchange-correlation functional. The action of the core electrons on the valence electrons was replaced by norm-conserving, fully relativistic pseudo potentials generated by the scheme of Troullier and Martins in the fully separable form [17];

the electronic wave functions were expanded in a plane-wave basis set. The used cut-off energy for the plane wave expansion of 50 Ry is sufficient to reliably give the adsorption energies, although the O-O interaction is not fully converged [18], even with a large pseudo potential core radius of $r_c^{l=0,1} = 1.45$ bohr; $l=1$ was used as the local component. The core radii for the Ru pseudo potential are $r_c^{l=0,2} = 2.48$ bohr and $r_c^{l=1} = 2.78$ bohr; $l=0$ was used as the local component [19]. The k-point sampling of the surface Brillouin zone was accomplished with an equidistant 8×10 point Monkhorst-Pack grid [20] in the (1×1) unit cell, giving 20 k-points in the irreducible part of the (1×1) Brillouin zone; special care was taken to ensure an equivalent sampling in all (surface) geometries studied. To stabilize the Brillouin zone integration the occupation numbers were broadened using a Fermi function with a width of 0.1 eV; the total energies were extrapolated to the case of no broadening. The surface was modeled using the supercell approach, using eight layers of Ru $(10\bar{1}0)$ and placing the O atoms on one side of this slab. We account for the difference of the asymptotic electrostatic potential by employing a surface dipole correction [21]. The calculation scheme allows for relaxation of the electrons and atoms, where we relaxed the positions of the O atoms and the atoms in the top two Ru layers, keeping the lower five Ru layer spacings fixed at the bulk values. A similar procedure has shown to work reliably for the case of nitrogen adsorbed on Ru (0001) [22].

III. RESULTS

A. LEED results

The analyses of the clean Ru $(10\bar{1}0)$ surface and the oxygen-induced $c(2 \times 4)$ -2O and (2×1) pg-2O overlayers were based on experimental data sets containing cumulative energy ranges of 2165 eV, 4525 eV, and 3621 eV, respectively. In comparison to the oxygen Co $(10\bar{1}0)$ system, one would not expect to find heavy reconstructions at the surface (recall that Ru is a much harder material than Co). Assuming only high-coordination adsorption sites for oxygen, we are left with eight essentially different models for the $c(2 \times 4)$ -2O structure as compiled in Fig. 2. The presence of the glide symmetry plane in the (2×1) pg-2O overlayer imposes constraints to the structure which further narrows down the number of possible models depicted in Fig. 3. We should note that the glide symmetry plane disappeared reversibly upon cooling below 230 K; this interesting issue will be the subject of a future paper [23]. For this reason we took the LEED IV data of the (2×1) pg-2O phase at 250 K.

The clean Ru $(10\bar{1}0)$ surface was analyzed first. Two different terminations of the $(10\bar{1}0)$ surface are possible, exhibiting different corrugations of about 0.8 Å (short termination) and 1.6 Å (long termination), re-

spectively. From a comparison with the surface geometries of Re $(10\bar{1}0)$ [24] and Co $(10\bar{1}0)$ [25], we anticipated that only the short-termination with a small corrugation will be the stable one. The measurements of LEED IV curves at 110 K turned out to be complicated, due to small amounts of contaminants arising from the residual gas adsorption, as the LEED IV curves changed quite substantially after a few minutes. Yet, using these IV curves for the LEED analysis, we ended with an optimum structure for which the topmost Ru layer spacing is almost bulk-like. This finding conflicts with the results of about 10 % contraction obtained for the topmost Re and Co layer distance on $(10\bar{1}0)$. The best fit was achieved with the expected short termination giving an overall Pendry R-factor of 0.25. From AES measurements, which indicated a clean surface, we concluded that very likely hydrogen, which is inevitably present in the residual gas, should be responsible for this effect. Therefore, we recorded a further set of LEED IV data at 430 K, a temperature at which hydrogen is not stabilized at the surface. With these new LEED data a much better fit to the experimental data was possible, *i. e.* $R_P = 0.18$, and in addition, the structural parameters were now consistent with corresponding results for Co and Re. The topmost Ru layer spacing turned out to be contracted by 10 ± 1.5 % followed by a small expansion of 2.5 % of the second Ru layer spacing in good agreement with the DFT calculations (cf. section 3.3). Structural investigations of the hydrogen adsorption on Ru $(10\bar{1}0)$ for various exposures are underway and will be presented in a forthcoming paper [26].

Next, we focus on the atomic geometry of the $c(2 \times 4)$ -2O phase on Ru $(10\bar{1}0)$. The various model structures considered in this LEED analysis are summarized in Fig. 2; all of these models provide at least one mirror plane across the densely-packed Ru rows in $[1\bar{2}10]$ direction. Only high-symmetry adsorption sites were tested. The best r-factors reached with these models are listed in Table 1, from which it becomes clear that the model with oxygen sitting in so-called hcp sites is preferred. The optimum adsorption geometry is presented in Fig. 4, and the agreement between experimental and calculated LEED data can be judged from Fig. 5; the overall r-factor is $R_P = 0.26$. The chemisorption of oxygen induces only small lateral (up to 0.05 Å) and vertical (up to 0.03 Å) displacements of atoms in the top double layer. The lateral arrangement of the oxygen atoms provides some clues about the interaction among the adsorbates. The oxygen atoms form zigzag chains along the troughs. Zigzag and zagzig chains are separated by an empty trough establishing the $c(2 \times 4)$ symmetry. The alternation of zigzag and zagzig chains is necessary to impose $c(2 \times 4)$ symmetry, otherwise a primitive (2×2) structure would have been formed. This indicates a long-range interaction between the O chains even across the densely-packed Ru trenches. The energy of this interaction is, however, quite small since at temperatures above 550 K the $c(2 \times 4)$ -O structure disorders as indicated by

LEED while the $(2\times 1)pg$ persists up to desorption. The appearance of empty troughs between consecutive zigzag chains, on the other hand, may be the result of the affinity of oxygen to bind to two Ru atoms in the topmost Ru layer without sharing these atoms with other O atoms. Last, the formation of zigzag chains even at low coverages indicates repulsion between the O atoms sitting on nearest-neighbor sites and attraction between next-nearest-neighbor sites. This arrangement maximizes the separation between oxygen atoms within the troughs, although the overall O-O separation is not maximized; from this point of view model hcp-c, cf. Fig. 2, would be more favorable. The bond lengths of oxygen to first-layer Ru atoms and second-layer Ru atoms is (2.08 ± 0.06) Å and (2.03 ± 0.06) Å, respectively. The contraction (10 %) of the topmost Ru layer spacing of the clean Ru $(10\bar{1}0)$ is partly lifted upon adsorption of oxygen, resulting in a contraction of about 4 %.

These structural characteristics of the $c(2\times 4)-2O$ phase are to be compared with the adsorption geometry of the second ordered oxygen overlayer, *i. e.* the $(2\times 1)pg-2O$. For modeling this oxygen overlayer, only three different models (Fig. 3) have to be considered. The corresponding optimum r-factors are compiled in Table 2. Clearly, also here the hcp site is most favored. The actual adsorption geometry determined by LEED is presented in Fig. 6, and a comparison between experimental and calculated LEED data is depicted in Fig. 7 (the overall r-factor is $R_P = 0.25$). The presence of the glide symmetry plane determines the lateral arrangement of the O atoms to consist again of O zigzag chains along the $[1\bar{2}10]$ direction. The main differences to the $c(2\times 4)-2O$ configuration are the absence of empty troughs and the exclusive occurrence of zigzag chains (and no zagzig chains). Therefore, the transformation of the $c(2\times 4)-2O$ into the $(2\times 1)pg-2O$ phase upon adding oxygen is accomplished by filling up the empty troughs by O zigzag chains and shifting every zagzig chain of the $c(2\times 4)-2O$ along the $[1\bar{2}10]$ direction by one lattice unit. In contrast to the $c(2\times 4)-2O$ surface, the high-coverage $(2\times 1)pg-2O$ phase is thermally very stable and exists up to desorption. Besides these general features of the oxygen arrangement, the bond lengths between oxygen and the first-layer and second-layer Ru atoms amount to 2.01 ± 0.06 Å and 2.04 ± 0.06 Å, respectively. As with the $c(2\times 4)-2O$, oxygen induces only little local reconstructions in the top Ru double layer. The topmost Ru layer spacing is now slightly expanded by 4 %.

B. HREELS Results

In order to study the vibrational properties of chemisorbed oxygen on Ru $(10\bar{1}0)$, HREEL spectra were recorded in a separate UHV apparatus. A characteristic set of spectra is shown in Fig. 8. The main energy loss is found at 64 to 67 meV and is assigned to the

Ru-O stretch mode perpendicular to the surface $\nu(\text{Ru-O})$. With progressing oxygen exposure, this mode shifts from 67 meV down to 64 meV. At an oxygen dose of 10 L, it broadens and obviously contains several contributions. The mode with a polarization perpendicular to the surface is expected to be observable with HREELS for a chemisorbed atom. The observed energy compares well with the value of 64 meV found for the low-coverage mode ($\theta_O = 0.25$) of atomic oxygen on Ru (0001) .

Between 70 and 100 meV, a broad band of losses is present, which exhibits peaks at 86 and 95 meV for the 2×1 structure. The loss at 95 meV occurs already for the smallest dose of 0.1 L. In analogy to the work of Mitchell and Weinberg [27], we tentatively assign these losses to subsurface oxygen. Mitchell and Weinberg observed a strong peak at 80 meV accompanied by a broad band between 80 and 130 meV with weak peaks at 92 and 102 meV, after dosing the oxygen-covered Ru (0001) surface at $\theta_O = 0.5$ with additional NO_2 . They interpreted this as the beginning of RuO_x formation. It should be noted, however, that a single loss at 81 meV can be prepared without any broad band at higher energies and that this spectrum is characteristic for the $(1\times 1)-O$ overlayer [28]; the atomic geometry of the latter was recently determined by total energy calculations and LEED [15]. From these observations we conclude that on Ru $(10\bar{1}0)$ - different to Ru (0001) - the oxygen atoms penetrate into the subsurface region right away from the beginning of oxygen exposure.

Besides the main $\nu(\text{Ru-O})$ stretch mode and the features at higher energies, peaks at 13–15, 23, 44 and 54 meV are also observed. These modes are here not analyzed in detail, but it is clear that they belong to phonons of the oxygen-modified Ru $(10\bar{1}0)$ surface and the translational modes of oxygen. For Ru (0001) it was recently discussed [28] that the change in symmetry with oxygen adsorption phonon bands can be folded back to the Γ point and can become visible in HREELS. The weak peak around 250 meV is assigned to the $\nu(\text{C-O})$ stretch mode from background CO.

C. DFT Calculations

The lattice parameters were calculated using the $(10\bar{1}0)$ plane as the base of the unit cell and filling the cell with four atomic layers according to the stacking sequence. The results obtained, $a = 2.78$ Å and $c/a = 1.58$, are very close to our values for the Ru (0001) surface, thus confirming a good k-point sampling. The overestimation of a by about 2 - 3 %, compared to the experiment, is found in DFT-GGA calculations for later 4d transition metals.

As, to the best of our knowledge, this is the first DFT calculation for the clean Ru $(10\bar{1}0)$ surface, we shall elaborate this issue here to some extent. The clean Ru surface was modeled using an eight-layer slab, and the two first

substrate layers were relaxed. The hcp ($10\bar{1}0$) surface is a more open surface than the hexagonal, close-packed (0001) surface, and there are two possible terminations. As expected (due to higher coordination of surface atoms and smaller surface corrugation), the short termination [outermost layer distance $d = 1/(2\sqrt{3}) \times c$] is energetically favored by $41 \text{ meV}/\text{\AA}^2$ over the long-terminated surface [$d = 1/\sqrt{3} \times a$]. The surface energy of the short termination is calculated as $176 \text{ meV}/\text{\AA}^2$ which is $\approx 15 \%$ larger than our DFT-GGA surface energy for the Ru (0001) surface ($154 \text{ meV}/\text{\AA}^2$). Note that DFT-GGA yields lower surface energies than DFT-LDA and it appears that LDA is in better agreement with experiments [29]. The relaxations of the first and second layer turned out to be $d_{12}/d_0 = -13.7 \%$ and $d_{23}/d_0 = -0.7 \%$, thus, a slightly larger inward relaxation is obtained than from the LEED intensity data ($d_{12}/d_0 \approx -10 \%$). Similar deviations have also been observed with Ru (0001) [30,31]. The inclusion of the effects of zero-point vibration and thermal expansion [32] in the calculations further reduces the difference between theory and experiment: at $T = 300\text{K}$ $d_{12}/d_0 = -12.3 \%$ which agrees with the experiments within the error bars. The calculated work function of 4.88 eV is somewhat too low compared to the experiment, 5.10 eV [33], again as also observed in DFT-GGA calculations of other metals [29].

To study the adsorption of oxygen, we have considered several coverages and overlay arrangements. They are compiled in Table 3, together with the adsorption energies per O atom and work function changes with respect to the clean surface. In addition to the experimentally observed surface structures, we also studied some hypothetical structures in order to gain additional information about the adsorbate-adsorbate interaction. From Table 3, we see that the adsorption energy decreases upon oxygen adsorption, while the work function increases. Even the (1×1) -2O phase is found to be stable. This is no surprise, as the oxygen atoms are bound on threefold hollow sites as on the Ru (0001) surface, and the density of adsorbates is close to the one in the Ru (0001)- (1×1) -O structure, which was also found to be stable [15,31]. Interesting is that the energetically lowest (1×1) -2O structure on Ru ($10\bar{1}0$) contains both atoms adsorbed on the hcp and fcc sites, whereas in the (1×1) -1O structure the hcp site is clearly preferred. The occupation of fcc and hcp sites in the (1×1) -2O phase maximizes the separation between the O atoms within the troughs and therefore minimizes the electrostatic O-O repulsion. Yet, the LEED experiments did not give evidence for the presence of a (1×1) -2O structure. Therefore, one might conjecture that the excess oxygen atoms partly penetrate into the subsurface region at a sample temperature of 550 K leading to the diffuse and streaky (1×2) LEED pattern.

Comparing the nearest-neighbor distance and the adsorption energy of the (2×1) pg-2O with the (1×1) -1O, we find the energy gain by forming zigzag chains to be 60 meV , which is consistent with a reduction of the O-O

repulsion. The binding energy per adsorbate increases by 220 meV per atom, when the coverage is reduced from 1 to $1/2$. However, the $c(2 \times 4)$ -2O structure, where the zigzag and zagzig chains alternate, is preferred over the (2×2) -2O exhibiting zigzag chains only. This might be related to a more favorable relaxation of the outermost Ru atoms in the trenches.

Next, we are focusing on the oxygen-Ru distances as a function of coverage. The O-Ru distances in the $c(2 \times 4)$ ($d[\text{O-Ru}(1)] = 2.09 \text{ \AA}$ and $d[\text{O-Ru}(2)] = 2.10 \text{ \AA}$) and the (2×1) pg structures ($d[\text{O-Ru}(1)] = 2.11 \text{ \AA}$ and $d[\text{O-Ru}(2)] = 2.11 \text{ \AA}$) are larger than in the experiment ($c(2 \times 4)$ -2O: $d[\text{O-Ru}(1)] = 2.08 \text{ \AA}/d[\text{O-Ru}(2)] = 2.03 \text{ \AA}$; (2×1) pg-2O: ($d[\text{O-Ru}(1)] = 2.03 \text{ \AA}$ and $d[\text{O-Ru}(2)] = 2.03 \text{ \AA}$)), which might be due to the DFT-GGA scheme. In disagreement with the experiments, the bond lengths vary only slightly, when going from the $c(2 \times 4)$ -2O to the (2×1) -2O structure; the LEED analyses show a notable and clear decrease of the O-Ru(1) bond length. Specific values for the atomic coordinates as determined by DFT-GGA calculations are indicated in Figs. 4 and 6. However, going to even higher O coverages, also DFT-GGA calculations indicate a decreasing O-Ru distance. DFT-GGA calculations of the system O/Ru (0001) [31, 34] show that the O-Ru bond strength decreases monotonically with increasing O coverage.

One should note that the Ru-O binding energy is the results of both the direct O-Ru interaction and the O-O repulsion. It is well possible that the direct O-Ru interaction increases with coverage (consistent with a shorter bond length) but the adsorption energy decreases, because of the electrostatic O-O repulsion. Unfortunately both contributions cannot be separated in the DFT calculations. A more detailed discussion of this effect as found with alkali metal adsorption on Al(111) may be found in Ref. 21.

Using the same pseudo potentials as for O/Ru ($10\bar{1}0$), the binding energies of oxygen on Ru (0001) turned out to be 3.08 eV and 2.29 eV and the Ru-O bond lengths are 2.07 \AA and 2.04 \AA in the (2×2) -O and the (1×1) -O phase, respectively. The slightly larger Ru-O binding energy in the Ru (0001)- (2×2) -O phase compared to Ru ($10\bar{1}0$)- $c(2 \times 4)$ -O is due to the larger O-O separation.

In addition to the above DFT-GGA calculations, we analyzed the binding of oxygen on Ru ($10\bar{1}0$) by using a simple tight-binding model [35], which we recently applied to N/Ru (0001) [22]. The qualitative result is the same (cf. Fig. 9) *i. e.*, the bond splits the mixed adsorbate-substrate orbitals - mainly O_{2p} and Ru_{4d} - into a bonding level below and an anti-bonding level above the Fermi level, emptying some Ru_{4d} orbitals just below the Fermi energy. The position of the bonding orbital shifts from $E_F - 5.5 \text{ eV}$ [$c(2 \times 4)$ -2O] to $E_F - 6.5 \text{ eV}$ [(1×1) -2O] with increasing coverage; the position of the bonding orbital does not shift, when going from the $c(2 \times 4)$ -2O to the (2×1) pg-2O. The anti-bonding peak is at $E_F + 1.5 \text{ eV}$ in the $c(2 \times 4)$ -2O structure and shifts slightly to higher energies when increasing the coverage. Both shifts are in

agreement with the smaller O-Ru distance upon increasing the O coverage (taken from Table 3), if one neglects the effective repulsion between the oxygen atoms.

IV. DISCUSSION

The interaction of oxygen with the substrate and neighboring oxygen atoms can be classified in three categories, which will be described in the sequence of their importance.

1. Oxygen binds to the Ru substrate via two atoms in the topmost Ru layer and one in the second layer. Such an adsorption site may also be the adsorption site in the limit of zero coverage. Obviously, oxygen prefers to form bonds to the low-coordinated Ru atoms of the topmost layer. According to Tersoff and Falicov [36], this adsorption behavior might be related to the local d-band of these Ru atoms. Since the coordination number of these atoms is smaller than that of the other Ru atoms, the local d-band is narrower (in the tight-binding model the band width is proportional to the square root of the coordination number) and since the Fermi level is located about in the middle of the band, the local density of states becomes larger. Accordingly, Ru atoms in the second layer (with the higher coordination) should have a smaller density of states than Ru atoms in the outermost layer. Using now simple effective medium theory (EMT) arguments, which have been put forward by Nørskov and coworkers [1a,37], the bonding between oxygen and Ru depends critically on the local charge density offered by the substrate: The more local charge density is available, the longer the O-Ru bond length (and the smaller is the Pauli repulsion). In fact, this situation is encountered with the $c(2\times 4)$ -2O overlayer. The bond length of O to Ru(1) with 2.08 Å is markedly longer than that between O and Ru(2) (2.03 Å). In addition, the O-induced reconstructions are much less pronounced on Ru(10 $\bar{1}$ 0) than on Ru(0001) [38]. This finding is consistent with the notion that oxygen atoms on Ru(10 $\bar{1}$ 0) can readily reach the optimum charge density without shifting the Ru atoms that much. The opposite is the case for Ru(0001), since all Ru atoms are high-coordinated and, therefore, the local charge density is low. Consequently, the O-Ru bond length of Ru(0001)-(2 \times 2)-O (2.03 Å [38]) is quite short and comparable to the O-Ru(2) value on Ru(10 $\bar{1}$ 0). Yet, this interpretation within the framework of local charge density is not conclusive, as the present DFT calculations (which are certainly superior over EMT calculations in terms of accuracy) cannot reconcile this behavior for reasons which are unknown: There is almost no variation in the O-Ru bond length with the number of O atoms coordinated to a Ru atom. DFT calculations do show that the hcp adsorption site of oxygen is favored by more than 0.2 eV over the fcc site (cf. Table 3, [1 \times 1]1O-fcc and [1 \times 1]1O-hcp).

2. The next important contribution to the Ru-O

bond establishes the formation of zigzag chains along the troughs. These zigzag arrangements were also observed for hydrogen on fcc(110) surfaces, such as Ni(110) [39] and oxygen on Rh(110) [40], and it therefore seems a quite common structural motif in surface science. LEED and HREELS measurements indicate that even at lower O coverages these chains are preferentially formed. This observation is also supported by the DFT calculations which indicated that the formation of zigzag chains is by 60 meV more favorable than single O atoms. This means that the interaction between the oxygen atoms along the zigzag chains is attractive. Albeit this attractive interaction, oxygen does not like to share attached Ru atoms with other oxygen atoms. This attribute is manifested by the empty trough between the zigzag chains observed in the $c(2\times 4)$ -2O system. If, however, the O coverage is increased, the empty troughs are filled up with the consequence that oxygen atoms share common Ru atoms in the topmost layer. Accordingly, the local charge density offered by Ru(1) atoms for each O atoms is smaller and, again using the simple effective medium theory of bonding, this tells us that now the oxygen atoms have to come closer to the surface to experience a similar local charge density as in the $c(2\times 4)$ -2O phase. In fact, this aspect has been identified in the LEED analysis, the bond lengths of O to Ru(1) change from 2.08 Å to 2.01 Å, when going from the $c(2\times 4)$ -2O to the (2 \times 1)-2O phase. The bonding between the oxygen atom and the coordinated Ru(2) atom is not affected by the presence of more oxygen on the surface, as evidenced by the unchanged bond length of 2.03 Å. These findings cannot be easily reconciled with simple arguments adopted from coordination chemistry, since there the bond length is directly related to the bond strength: The weaker the bonding, the longer the respective bond length. The present DFT calculations show, however, that the binding energy of oxygen is reduced by about 220 meV, when the oxygen coverage is increased so that two oxygen atoms have to share one Ru atom in the topmost layer. Accordingly, the O-Ru(1) and O-Ru(2) bond lengths should increase which, however, is not observed experimentally. One should recall that the Ru-O binding energy is composed of the direct O-Ru interaction and the O-O repulsion. It is conceivable that the direct O-Ru interaction increases with coverage (consistent with a shorter bond length) but the adsorption energy decreases, because of the electrostatic O-O repulsion. Since we are not able to entangle these two contributions in our DFT calculations this argument remains elusive.

Unfortunately, the present DFT calculations are not able to elaborate on this point, as the optimum bond length turned out not to change with O coverage when the $c(2\times 4)$ -2O phase transforms into the (2 \times 1)pmg-2O phase. It could be that such an effect is beyond the capability of state-of-the-art DFT-GGA calculations. As possible sources for this discrepancy we mention just the exchange correlation term, the frozen-core approximation, the linearization of the core-valence exchange cor-

relation and the transferability of the pseudopotentials in our DFT calculations. Although the variation of the Ru(1)-O bond length with O-coverage (as determined by LEED) is similar to the quoted error bars for the Ru(1)-O bond lengths, simple probability arguments, *i. e.* taking the product probability, tell that the found variation is statistically significant. A simple calculation shows that the probability to find the Ru(2)-O bond length to increase is only 20 %.

An alternative explanation for the observed shortening of the Ru(2)-O bond length with O-coverage could be that with increasing O coverage the ionicity of O decreases. Consequently, the Pauling radius of oxygen would shrink consistent with a smaller Ru-O bond length. This explanation fails however to explain the observed change of work function $\Delta\phi$. Using ultraviolet photoelectron spectroscopy [41] it was shown that $\Delta\phi$ increases from 0.49 eV [c(2x4)-2O] to 1.12 eV [(2x1)pg-2O] with respect to the clean surface. This super-linear increase of the oxygen induced dipole moment conflicts with a reduced degree of ionicity in combination with a smaller Ru-O bond length, *i. e.* smaller dipole length. It is worth mentioning that this super-linear change of the work function induced by oxygen is nicely reproduced by the present DFT calculations. Drastic changes in the oxygen induced dipole moment with coverage signifies the importance of the electrostatic repulsion between the O atoms. It might be that this adsorbate-adsorbate interaction give a clue to the experimentally observed shortening of Ru-O bond length (cf. the discussion in Ref. [21]).

A quite similar effect has recently been observed for oxygen on Ru (0001) [15]. While the O-Ru bond length in both the (2x2) and the (2x1) phase was 2.03 Å [38], this bond length shortens to 2.00 Å for the (1x1)-O structure, although the binding energy decreases by more than 0.8 eV, as evidenced by DFT calculations. Obviously, local coordination chemistry considerations, which would predict that the stronger the bond, the shorter the bond length, are inadequate to account for the bonding of oxygen atoms at the Ru surfaces. Interestingly, on Ru (0001) the ν (Ru-O) stretch mode energy increases with oxygen coverage, as found by recent HREELS study on Ru (0001) [28]. Hence, the Ru-O potential well obviously becomes steeper, when the Ru-O distance decreases.

On Ru (10 $\bar{1}$ 0) the Ru-O stretch mode changes its energy only slightly from 67 to 64 meV with coverage, *i. e.*, the steepness of the potential normal to the surface does not change very much. The frequency is very close to that one for the low-coverage oxygen phase on Ru (0001) (64 meV at $\theta_O = 0.25$). Only when the lateral nearest-neighbor O-O distance on Ru (0001) changes from 5.72 Å ($\theta_O = 0.25$) to 2.71 Å, the ν (Ru-O) mode energy changes to 71 meV ($\theta_O = 0.50$) and 81 meV ($\theta_O = 1.00$) [28]. For Ru (10 $\bar{1}$ 0) the nearest-neighbor distances remain quite large in both phases: 3.30 Å in the c(2x4)-2O and 3.38 Å in the (2x1)-2O. Therefore, the ν (Ru-O) mode energy is nearly constant. The small change from 67 meV to 64 meV goes along with an increase of the

nearest-neighbor distance, similar to the effect observed with Ru (0001).

Finally, we like to note that for oxygen, in contrast to N and H on Ru (10 $\bar{1}$ 0), basically only the mode perpendicular to the surface is visible. For N [42] and H [43] at least one translational mode was observed in addition. We conclude that for oxygen the bond is more symmetrical, with respect to the surface normal, than for N and H. This conclusion is also supported by recent LEED analyses of H on Re(10 $\bar{1}$ 0) and Ru (10 $\bar{1}$ 0), where the short-bridge site has been identified [26].

From the HREELS results - that the O against Ru vibration frequency shifts from 67 meV to 64 meV, when going from the c(2x4)-2O to (2x1)pg-2O - one can learn that the potential perpendicular to the surface varies more softly in the (2x1)pg-2O than in the c(2x4)-2O phase. This might be attributed to the smaller bond strength of oxygen to the Ru surface in the (2x1)pg-2O than in c(2x4)-2O, as indicated by the present DFT calculation.

3. The smallest interaction energy is that which determines the correlation between the zigzag chains in the c(2x4)-2O phase. This interaction can easily be overcome by increasing the surface temperature above 550 K or simply adding more oxygen to the surface. DFT calculations indicate that this energy contribution is with 60 meV indeed quite small [cf. Table 3: c(2x4)-2O and (2x2)-2O].

V. SUMMARY

The c(2x4)-2O and the (2x1)pg-2O phases on Ru (10 $\bar{1}$ 0) were characterized by using quantitative LEED, DFT-GGA calculations and HREELS. We have shown that in both phases oxygen atoms occupy the threefold coordinated hcp site along the densely packed rows on an otherwise unreconstructed surface, *i. e.*, the O atoms are attached to two atoms in the first Ru layer Ru(1) and to one Ru atom in the second layer Ru(2). With LEED we found that in the low-coverage c(2x4)-O phase the bond lengths of O to Ru(1) and Ru(2) are 2.08 Å and 2.03 Å, respectively, while corresponding bond lengths in the high-coverage (2x1)-2O phase are 2.01 Å and 2.04 Å. The shortening of the Ru(1)-O bond length with O coverage may be a consequence of the competition for electron charge density, although this aspect could not be reconciled by our DFT calculations. The presence of empty troughs in the c(2x4)-2O phase indicates that oxygen atoms do not like to share Ru atoms in the topmost layer with other O atoms. DFT calculations show that the energy per O atom in both phases differs by 220 meV. The energy gain of 60 meV drives the O atoms to build zigzag chains along the troughs instead of a dispersed O-phase. A similar energy contribution is gained when forming alternating zigzag and zagzig chains instead of zigzag chains only. HREEL spectra reveal a loss

at 67 meV [$c(2\times 4)$ -2O] and 64 meV [(2×1) pg-2O], which is assigned to the $\nu(\text{Ru-O})$ stretch mode. The small variation in frequency with O coverage [compared to a much bigger shift for the oxygen phases on Ru(0001)] reflects the similar lateral arrangements of oxygen in both phases on Ru(10 $\bar{1}$ 0), *i. e.* the formation of zigzag chains.

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VII. FIGURE CAPTIONS

FIG. 1. LEED patterns of the a) clean Ru(10 $\bar{1}0$), b) Ru(10 $\bar{1}0$)-c(2 \times 4)-2O, and c) Ru(10 $\bar{1}0$)-(2 \times 1)pg-2O.

FIG. 2. Possible structure models for the Ru(10 $\bar{1}0$)-c(2 \times 4)-2O, which were tested by LEED calculations.

FIG. 3. Possible structure models for the Ru(10 $\bar{1}0$)-(2 \times 1)pg-2O, which were tested by LEED calculations.

FIG. 4. The atomic coordinates for the best-fit model of c(2 \times 4)-2O as obtained by quantitative LEED and DFT-GGA calculations. Oxygen atoms reside in hcp-like adsorption sites forming zigzag chains along the troughs. Zigzag and zagzig chains are separated by empty troughs so that no oxygen atom has to share a Ru atom in the topmost layer with neighboring O atoms. The oxygen bond lengths to first-layer and second-layer Ru atoms are 2.08 Å and 2.03 Å, respectively.

FIG. 5. Comparison of experimental and theoretical LEED IV data for the best-fit model of the c(2 \times 4)-2O phase on Ru(10 $\bar{1}0$) (cf. Fig. 4). The overall R_p -factor is 0.26.

FIG. 6. The atomic coordinates for the best-fit model of (2 \times 1)pg-2O, as determined by LEED and DFT. Oxygen atoms reside in hcp-like adsorption sites forming zigzag chains along the troughs. The oxygen bond lengths to first-layer and second-layer Ru atoms are 2.01 Å and 2.04 Å, respectively.

FIG. 7. Comparison of experimental and theoretical LEED IV data for the best-fit model of the (2 \times 1)pg-2O phase on Ru(10 $\bar{1}0$) (cf. Fig. 6). The overall R_p -factor is 0.25.

FIG. 8. HREEL spectra for a series of oxygen exposures on Ru(10 $\bar{1}0$) at room temperature. The exposures and the monitored LEED patterns are indicated in the figure. All spectra are recorded in specular geometry with primary energy of 2.5 eV. The scaling factor in the loss region is 100.

FIG. 9. The difference in density of states, $n(\text{Ru}+\text{O}) - n(\text{Ru})$, where $n(\text{Ru}+\text{O})$ is the density of states of

the adsorbate system Ru(10 $\bar{1}0$)-(2 \times 1)pmg-O (dotted-dashed line), Ru(10 $\bar{1}0$)-(1 \times 1)-(fcc+hcp)2O (solid line), Ru(10 $\bar{1}0$)-c(2 \times 4)-2O (dotted line) and $n(\text{Ru})$ that of the clean Ru surface. The one-electron eigenvalues are broadened by 0.6 eV.

VIII. TABLES

Table 1: Optimum Pendry-r-factors obtained for different models of the Ru(10 $\bar{1}0$)-2O-c(2 \times 4). The total energy range is 4525 eV (2445 eV fractional-order, 2080 eV integer-order beams).

adsorption sites	R_p		
	total	integer	fractional
fcc A	0.65	0.30	0.94
fcc B	0.66	0.30	0.94
fcc C	0.66	0.29	0.96
hcp A	0.26	0.20	0.33
hcp B	0.57	0.30	0.83
hcp C	0.50	0.24	0.76
long bridge	0.74	0.39	1.02
short bridge	0.68	0.42	0.91

Table 2: Optimum Pendry-r-factors obtained for different models of the Ru(10 $\bar{1}0$)-2O-(2 \times 1)p2mg. The total energy range is 3621 eV (1464 eV fractional-order, 2157 eV integer-order beams).

adsorption sites	R_p		
	total	integer	fractional
fcc	0.71	0.55	0.95
hcp	0.25	0.23	0.29
short bridge	0.69	0.56	0.87

Table 3: Oxygen adsorption energy, work function change and O-Ru distances in different overlayer structures. The adsorption energy is calculated with respect to a free oxygen molecule. Ru(1) denotes the outermost-layer Ru atoms and Ru(2) the second-layer atoms. In the structure (1 \times 1)-2O (hcp-fcc) we give the average of the distances from the atom at the hcp/fcc site to the Ru atoms.

structure	coverage	E_{ad} (eV)	$\Delta\phi$ (eV)	$d[\text{O-Ru}(1)]$ (Å)	$d[\text{O-Ru}(2)]$ (Å)
c(2 \times 4)-2O	0.50	2.81	0.69	2.09	2.10
(2 \times 2)-2O	0.50	2.75	0.65	2.08	2.11
(2 \times 1)-1O	0.50	2.75	0.69	2.07	2.14
(2 \times 1)pmg-2O	1.00	2.59	1.61	2.11	2.11
(1 \times 1)-1O hcp	1.00	2.53	1.16	2.07	2.09
(1 \times 1)-1O fcc	1.00	2.30	0.74	2.04	2.11
(1 \times 1)-2O hcp	2.00	1.37	1.33	2.01	2.10
(1 \times 1)-2O hcp-fcc	2.00	1.47	1.91	1.98	2.08