Theoretical study of O adlayers on Ru(0001)

C. Stampfl and M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany
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Recent experiments performed at high gas partial pressures indicate that ruthenium can support unusually high concentrations of oxygen at the surface. To investigate the structure and stability of high coverage oxygen structures, we performed density functional theory calculations, within the generalized gradient approximation, for O adlayers on Ru(0001) from low coverage up to a full monolayer. We achieve quantitative agreement with previous low-energy electron diffraction intensity analyses for the (2×2) and (2×1) phases and predict that an O adlayer with a (1×1) periodicity and coverage $\Theta=1$ can form on Ru(0001), where the O adatoms occupy hcp-hollow sites. [S0163-1829(96)06528-9]

I. INTRODUCTION

The interaction of oxygen with metal surfaces forms the basis of many technologically important processes, for example, bulk oxidation, corrosion, and heterogeneous catalysis. It is therefore of great interest to obtain a detailed understanding of the changes in the atomic and electronic structure that oxygen adsorption often induces due to the formation of strong chemical bonds.[1,2] The behavior of O on metal surfaces is quite varied and depends markedly on the coverage and temperature, and on the orientation of the surface of the particular metal. Generally, the close-packed surfaces are more stable against reconstruction; often, however, significant atomic relaxations of the substrate are induced by O adsorption.[1] At higher coverages of oxygen, at elevated temperatures, oxidelike structures can form on a number of metal surfaces.[2]

From recent experiments of the catalytic oxidation of carbon monoxide, performed at high gas partial pressures, there is evidence that Ru(0001) can support unusually high concentrations of oxygen at the surface.[3,4] In order to investigate the structure and stability of high-coverage oxygen structures, we performed density functional theory calculations for various O adlayers on Ru(0001). In particular, for the two ordered phases, (2×2) (Ref. 5) and (2×1) (Ref. 6), which form at room temperature under ultrahigh vacuum (UHV) conditions for coverages $\Theta=1/4$ and 1/2, respectively, as well as for an artificial (2×2) adlayer containing three oxygen atoms per unit cell with coverage $\Theta=3/4$, and for several higher-coverage (1×1) structures with coverage $\Theta=1$. Here, Θ is defined to be the ratio of the number of adsorbate atoms to the number of atoms in an ideal substrate layer. Calculations for the (2×2) and (2×1) phases provide a test of the accuracy of the calculations through comparison with low-energy electron diffraction (LEED) intensity analyses. From such comparisons it is found that very good agreement with respect to the preferred adsorption site and the obtained structural parameters is obtained. The calculations reveal that although a (1×1) phase is not observed to form under UHV conditions using molecular oxygen, perhaps due to the presence of activation energy barriers for dissociation of O_2, the adsorption of O in a (1×1) adlayer structure with coverage $\Theta=1$ is exothermic and should be able to form when energy barriers can be overcome or atomic oxygen is offered.

II. CALCULATION METHOD

We use density functional theory (DFT) and the generalized gradient approximation (GGA) of Perdew *et al.*[7] for the exchange-correlation functional. The surface is modeled using the supercell approach where we use a (2×2) surface unit cell for all coverages investigated and four layers of Ru(0001) with a vacuum region corresponding to thirteen such layers. The O atoms are adsorbed on one side of the slab and the field thus introduced is taken into account following the approach of Neugebauer and Scheffler.[8] *Ab initio*, fully separable pseudopotentials, created by the scheme of Troullier and Martins[9] are used, in which the GGA is employed for all atoms. Relativistic effects are taken into account for the Ru atoms by using spin-averaged potentials. The electronic wave functions are expanded in a plane-wave basis set where the energy cutoff is taken to be 40 Ry with three special **k** points in the surface Brillouin zone.[10] To check convergence, we also performed calculations using a higher-energy cutoff of 60 Ry and 14 **k** points in the irreducible part of the surface Brillouin zone of a (1×1) surface unit cell. In the calculation scheme[11] the position of the atoms is relaxed using damped molecular dynamics. We relax the positions of the O atoms and the Ru atoms in the top two layers, keeping the lower two Ru layers fixed.

III. CLEAN AND O/Ru(0001)

A. Clean Ru(0001)

For Ru bulk the theoretically obtained lattice constant is determined to be $a=2.754$ Å and the c/a ratio 1.587. Zero point vibrations are not considered in these (and later) theoretical results. The experimental values are $a=2.704$ Å and $c/a=1.584$.[12] We note that the a value obtained by our DFT-GGA calculation is $\sim2\%$ larger than the experimental result. This may be due in part to the use of pseudopotentials. The increase of the GGA result compared to that obtained using LDA (see below) is about 1.7% which appears to be comparable to that obtained in other studies,[13–18] although for transition metals only few GGA calculations exist; see for ex-

ample, Refs. 16–18. The topmost Ru-Ru interlayer spacing of Ru(0001) is found to be contracted by 2.5%, which is close to LEED-determined values of 2.3% (Ref. 19) and 2.1% (Ref. 20). The second interlayer spacing is calculated to be expanded by 0.7%. For these calculations we used a 60-Ry cutoff and fourteen special **k** points in the irreducible part of the Brillouin zone of a (1×1) surface unit cell and relaxed the top two Ru layers. The LEED analysis of Ref. 20 determines multi-layer relaxations corresponding to -0.1%, $+0.5\%$, -0.1%, and -0.6% for the second, third, fourth, and fifth interlayer spacings, respectively, where the minus sign represents a contraction and the plus sign an expansion. Previous DFT calculations that employed the local density approximation (LDA) obtained values of 3.9% (Ref. 21) and 4.0% (Ref. 20) for the first layer contraction when using the linear muffin-tin orbital and linear augmented plane wave (LAPW) methods, respectively. In the former study an fcc(111) structure was assumed for ruthenium and just the first interlayer spacing was relaxed. In the latter study, the two topmost interlayer spacings were relaxed where the second interlayer was found to be expanded by 0.7%. The magnitude of the contraction of the first interlayer spacing has been in fact a controversial issue.[20,22] In particular, it was suggested that hydrogen contamination was responsible for the smaller values reported from LEED intensity analyses as compared to *ab initio* calculations;[20] this suggestion was subsequently strongly refuted.[22] Using DFT-LDA, our bulk lattice constant a is found to be 2.718 Å and the c/a ratio 1.580 ($c=4.294$ Å). These values of a and c are 0.6% and 1.3% larger, respectively, than those obtained by the LAPW calculations of Feibelman *et al.*[20] These differences are small and not relevant for the present study, and are similar to the recent results obtained for Rh.[23] They might be due to the different treatments of relativistic effects and core electrons in the two methods. A contraction of 3.4% and an expansion of 0.2% are obtained for the first and second interlayer spacings, respectively. The GGA appears to bring about some improvement in the magnitude of the contraction for the first Ru-Ru interlayer spacing of the Ru(0001) surface with respect to that determined from experimental. We note, however, for the determination of multilayer relaxations that our slab is very thin and that the main goal of our study is in fact not the surface relaxation but the adsorption of oxygen.

B. (2×2)-O/Ru(0001)

We performed calculations for O in the fcc-hollow site (no atom in the layer beneath the site) and in the hcp-hollow site. From our calculations we find that the hcp-hollow site is energetically clearly favorable. This is in agreement with the site determined by a dynamical LEED intensity analysis.[5] The binding energy of O [relative to a free O atom, for which we included the spin polarization energy of 1.521 eV (Ref. 24)] in the hcp hollow site is 5.55 eV and in the fcc-hollow site it is 5.12 eV (see Table I).

TABLE I. Binding energies (in eV) of O on Ru(0001), relative to the free O atom, for the surface structures investigated. The binding energy differences, ΔE, defined relative to the value for the respective hcp-hollow sites, are also given.

Structure	Coverage	fcc-hollow site	hcp-hollow site	ΔE
(2×2)	0.25	5.12	5.55	0.43
(2×1)	0.5	5.00	5.28	0.28
(1×1)	1	4.76	4.84	0.08

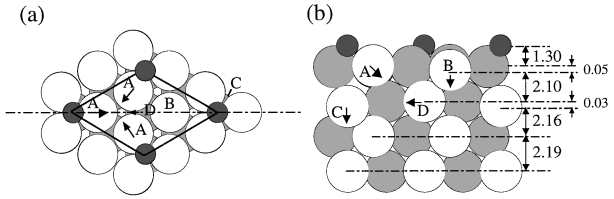

FIG. 1. Top view (a) and side view (b) of the atomic geometry of (2×2)-O/Ru(0001). The arrows (not drawn to scale) indicate the direction of the displacements of the substrate atoms with respect to the bulk positions. The dashed line in (a) indicates the plane of the cross section used in (b). Small dark grey circles represent oxygen atoms and large white and grey circles represent Ru atoms, where the latter correspond to those lying in the next plane. Interlayer spacings are given in ångstroms.

The atomic geometry of (2×2)-O/Ru (0001) is displayed in Fig. 1. In Table II we compare the calculated structural parameters with those obtained by the LEED intensity analysis.[5] Rather than giving a detailed description of the comparison of all the substrate relaxations, we simply refer to Table II, from which the high level of agreement with the LEED analysis can immediately be assessed. The calculated O-Ru bond length of 2.10 Å is somewhat longer than the LEED-determined value of 2.03 Å. The first Ru-Ru interlayer spacing is found to be contracted by 2.7% with respect to the bulk value (using the centers of gravity of the first and second buckled Ru layers). This agrees well with the value determined from the LEED analysis of 2.1%. The contraction of the top interlayer spacing of the clean surface is therefore not removed by oxygen adsorption at a quarter of a monolayer.

C. (2×1)-O/Ru(0001)

At half a monolayer of oxygen a (2×2) LEED pattern is observed experimentally, which corresponds to three rotated domains, each of (2×1) periodicity.[6] We performed calculations for O in the fcc- and hcp-hollow sites. The hcp-hollow site is again energetically the most favorable site with a binding energy of 5.28 eV; that for the fcc-hollow site is 5.00 eV (see Table I). The energetical preference of the hcp

TABLE II. Structural parameters for (2×2)-O/Ru(0001) with O in the hcp-hollow site. The lateral and vertical relaxations with respect to the bulk positions of the atoms A, B, C, and D (see Fig. 1) are denoted as $\Delta d_{\parallel}$ and Δd_z, respectively. The units are in ångstroms.

	(2×2)-O/Ru(0001)					
	O-Ru	$\Delta d_{\parallel}(A)$	$\Delta d_{\parallel}(D)$	$\Delta d_z(B)$	$\Delta d_z(C)$	
LEED	2.03	0.09	0.01	-0.05	-0.12	-0.08
DFT-GGA	2.10	0.07	0.01	-0.04	-0.09	-0.03

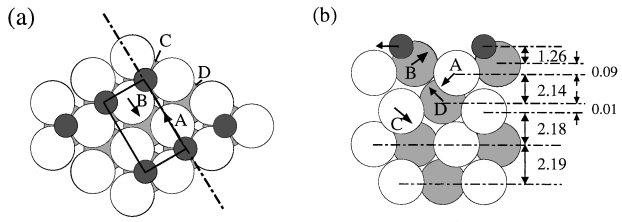

FIG. 2. Top view (a) and side view (b) of the atomic geometry of (2×1)-O/Ru(0001). The arrows (not drawn to scale) indicate the direction of the atomic displacements. The dashed line in (a) indicates the plane of the cross section used in (b). Small dark grey circles represent oxygen atoms and large white and grey circles represent Ru atoms, where the latter correspond to those lying in the next plane. Interlayer spacings are given in ångstroms.

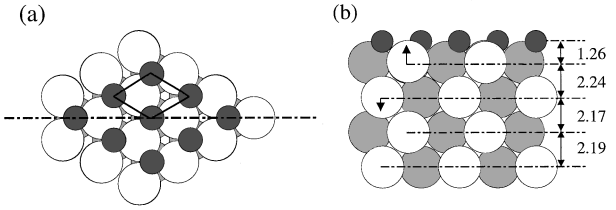

FIG. 3. Top view (a) and side view (b) of the atomic geometry of (1×1)-O/Ru(0001) with O in the hcp-hollow site (obtained with a 60-Ry cutoff and fourteen special **k** points in the irreducible part of the Brillouin zone). The arrows (not drawn to scale) indicate the direction of the displacements of the substrate atoms with respect to the bulk positions. Small dark grey circles represent oxygen atoms and large white and grey circles represent Ru atoms, where the latter correspond to those lying in the next plane. Interlayer spacings are given in ångstroms.

hollow site for O in the (2×1) structure is in accord with the LEED determination for the adsorption site.[6]

The atomic structure of (2×1)-O/Ru (0001) is depicted in Fig. 2. The O atoms adsorb in ''off'' hcp hollow sites; i.e., they are displaced slightly from the center of the hcp-hollow site towards an on-top site. In addition, complex relaxations of the substrate occur, including ''row-pairing'' and buckling of the substrate layers. The determined O-Ru bond length, and the lateral and vertical relaxations are given in Table III where they are compared with the results obtained from the LEED analysis.[6] Again, it can quickly be seen that quantitative agreement is achieved. We do note one deviation, however: The direction of the lateral displacement of atom D, $\Delta d_{\parallel}(D)$ in Table III, has the opposite sign. That is, we obtain row pairing of the Ru atoms in the *second* Ru layer, as well as in the first layer, and the LEED analysis does not. We found that relaxing the third Ru layer does not change this result. The O-Ru bond length of 2.08 Å is similar to that which we determined for the lower coverage (2×2) structure of 2.10 Å. The value is again somewhat larger than that of 2.02 Å as obtained from the LEED intensity analysis. The first two Ru-Ru interlayer spacings, defined with respect to the centers of gravity of the buckled atomic layers, correspond to the bulk value to within 0.01 Å, for both the DFT-GGA and LEED results.

It is well known that calculated total-energy differences are typically much more reliable than the total energies themselves. This is due to the fact that in the difference, the errors (e.g., those due to the GGA) are reduced considerably. This is the reason that our calculated surface geometries are in good agreement with those obtained by LEED, even though our bulk lattice constant is $\sim2\%$ too large.

TABLE III. Structural parameters for (2×1)-O/Ru(0001) with O in the hcp-hollow site. The lateral and vertical relaxations with respect to the bulk positions of the atoms A, B, C, and D (see Fig. 2) are denoted as $\Delta d_{\parallel}$ and Δd_z, respectively. The units are in ångstroms.

		(2×1)-O/Ru(0001)			
	O-Ru	Δd_z (A)	Δd_z (B)	Δd_z (C)	Δd_z (D)
LEED	2.02	−0.03	0.04	−0.01	0.02
DFT-GGA	2.08	−0.05	0.04	−0.003	0.003
	$\Delta d_{\parallel}$ (O)	$\Delta d_{\parallel}$ (A)	$\Delta d_{\parallel}$ (B)	$\Delta d_{\parallel}$ (C)	$\Delta d_{\parallel}$ (D)
LEED	−0.06	−0.07	0.05	0.05	0.04
DFT-GGA	−0.02	−0.01	0.08	0.01	−0.01

D. (1×1)-O/Ru(0001)

We now investigate the structure and stability of (1×1)-O adlayers with coverage $\Theta=1$. Similarly to the lower-coverage structures we performed calculations for O in the fcc- and hcp-hollow sites. The obtained binding energies are given in Table I. The hcp-hollow site is energetically preferred with a binding energy of 4.84 eV and the fcc-hollow site has a binding energy of 4.76 eV. Thus the hcp-hollow site is favored, but at this coverage only by 0.08 eV. To check the convergence, we performed calculations using a higher-energy cutoff of 60 Ry with fourteen special **k** points in the irreducible part of the Brillouin zone of a (1×1) surface unit cell for the fcc- and hcp-hollow sites, as well as for the on-top and bridge sites. Similarly, for these calculations it is found that the hcp-hollow site is energetically more favorable, in this case by 0.06 eV. The atomic geometry of (1×1)-O/Ru(0001) is shown in Fig. 3. The O-Ru bond lengths, structural parameters, and binding energies for O in the fcc- and hcp-hollow sites, for calculations using both 40- and 60-Ry cutoffs, are collected in Table IV. It is noticeable that the O-Ru bond length of 2.03 Å is slightly shorter than that of the lower coverage structures. The first Ru-Ru interlayer spacing is found to be *expanded* by 2.7%. As can be seen from Table IV, the binding energies and the structural parameters obtained for the different basis sets differ by a maximum of 0.05 eV and 0.04 Å , respectively.

The value of the binding energy of O in the hcp-hollow site on Ru(0001) at coverage $\Theta=1$ shows that the adsorption is exothermic and indicates that the (1×1) adlayer structure should be able to form. That is, the binding energy is larger (by $\sim$ 1.8 eV per atom) than that which the O atoms have in O_2. The binding energy per O atom in O_2 is calculated to be 3.064 eV (obtained using a 60-Ry cutoff and a cubic cell of side length 15 bohrs) where the spin polarization energies of 1.521 eV (Ref. 24) for the free O atom and 0.913 eV (Ref. 24) for the O_2 molecule have been taken into account. The experimental result for the O_2 binding energy is 5.12 eV (or

TABLE IV. Structural parameters for (1×1)-O/Ru(0001) with O in the hcp- and fcc-hollow sites. O-Ru, d_z, and E_b represent, the O-Ru bond length, the interlayer spacings (in ångstroms), and binding energy (in eV), respectively.

	(1×1)-O/Ru(0001) hcp-hollow site					
	O-Ru	$d_{z,1}$	$d_{z,2}$	$d_{z,3}$	$d_{z,\text{bulk}}$	E_b
DFT-GGA (40 Ry)	2.04	1.28	2.27	2.19	2.19	4.84
DFT-GGA (60 Ry)	2.03	1.26	2.24	2.17	2.19	4.87
	(1×1)-O/Ru(0001) fcc-hollow site					
DFT-GGA (40 Ry)	2.05	1.29	2.33	2.13	2.19	4.76
DFT-GGA (60 Ry)	2.03	1.27	2.29	2.13	2.19	4.81

2.56 eV per O atom).[25] Under UHV conditions, however, experiments indicate that the (2×1) phase is the terminal one. We therefore conclude that the reason the (1×1) structure does not form under UHV conditions is due to a kinetic hindering of the dissociation of O_2 induced by the (2×1) adlayer. Interestingly, on a *stepped* Ru(0001) surface, the formation of a (1×1) structure for coverage $\Theta=1$ has been reported, which is stable to 600 K.[26] On the stepped surface, it is possible that step edges may act as sites over which dissociation of O_2 can occur. If atomic, as opposed to molecular, oxygen would be used we predict that the (1×1) phase will also be observed on Ru(0001) under UHV. This theoretical result could have implications for heterogeneous catalytic reactions in which dissociative adsorption of O_2 is a necessary reaction step (often rate limiting) in that if atomic oxygen would be used the kinetics may be greatly altered; it also raises the question if other higher-coverage surface structuress may be prepared with atomic sources of adsorbates.

IV. COVERAGE DEPENDENCE

As we have seen from above, the hcp-hollow site is the preferred adsorption site for O on Ru(0001) at all the coverages investigated. This is consistent with the trend that strongly chemisorbed chalcogen atoms on transition-metal surfaces usually occupy the site that the next substrate layer would occupy.[1,5,27] As noted above, we also performed calculations for a structure with coverage $\Theta=3/4$. In this structure O atoms are placed in hcp-hollow sites in the (2×2) surface unit cell. The O-Ru bond length is 2.07 Å , which is similar to that of the two lower coverage structures, and the first Ru-Ru interlayer spacing is expanded by 1.8%. From the coverage dependence of the binding energy as listed in Table I, it can be seen that the binding energy becomes less favorable with increasing coverage, which reflects a repulsive interaction between the adsorbates and implies that no island formation is expected to occur in the coverage regime of $\Theta=1/4$ to 1. Concomitantly, the difference in binding energy between the fcc- and hcp-hollow sites becomes less. In fact, for the full monolayer this difference is very small. Because the full monolayer is reached successively via the other (lower coverage) phases, for which the hcp site is clearly favored, we expect a nearly perfect hcp-site occupation, i.e., only few fcc-site dislocation structures, for the (1×1) oxygen layer.

To gain qualitative insight into the nature of the O-Ru bond we show in Fig. 4(a) the work function change as a function of coverage. It can be seen that there is a significant increase in the work function reflecting electron transfer from the substrate towards the O adatoms, in accordance with the high electronegativity of oxygen. The experimental results of Surnev, Rangelov, and Bliznakov[28] are included for comparison where good agreement between theory and experiment is obtained. Figure 4(b) shows the corresponding induced surface dipole moment where we note one unusual result: With increasing coverage from $\Theta=1/4$ to 1/2 the surface dipole moment *increases* whereas simple arguments would suggest that the O-O repulsion goes together with a depolarization leading instead to a decrease. In fact, this unusual result had been noted previously in experimental studies[26,28,29] and was taken as an indication of a possible change of the binding site or state of the adatom. The theory reproduces this dipole moment increase but does not find a

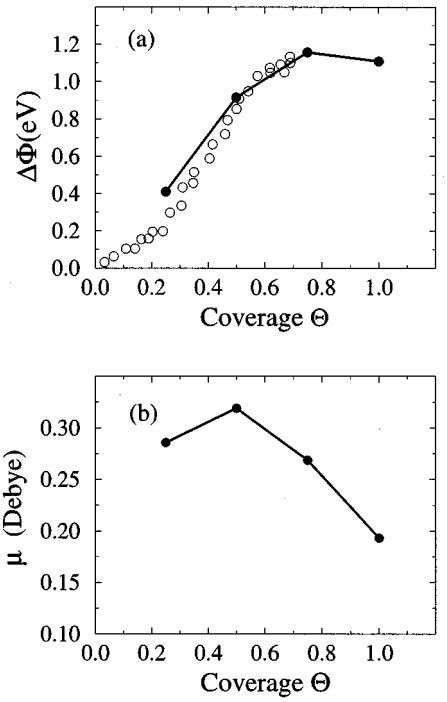

FIG. 4. Work-function change (a) and dipole moments (b) for O on Ru(0001) as a function of coverage Θ. Oxygen atoms occupy the hcp-hollow sites. Experimental results (Ref. 28) are shown as open circles.

site change. However, the nature of bonding is different in the $\Theta = 1/4$ and 1/2 phases. Whereas in the $\Theta = 1/4$ layer the symmetry is C_{3v}, which implies that the oxygen $2p_x$ and $2p_y$ states belong to the same group representation, the $\Theta = 1/2$ phase has a lower symmetry and removes the p_x, p_y degeneracy. This reduced symmetry is also reflected by the substrate distortions. For higher coverages, $\Theta = 1/2$ to $\Theta = 1$, the dipole moment decreases, implying a depolarization of the induced surface dipole where there is a transfer of electron density back from the adatoms towards the substrate to reduce the repulsive dipole-dipole interaction between the partially negatively charged O adatoms.

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