Theoretical study of O adlayers on Ru (0001)

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Recent experiments performed at high 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.

PACS numbers: 68.35.-p, 82.65.My

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]. On Zr, the O atoms apparently form an underlayer[3] even for the close-packed (0001) surface. At higher coverages of oxygen, at elevated temperatures, oxide-like structures can form on a number of metal surfaces[2].

From recent experiments of the catalytic oxidation of carbon monoxide, performed at high pressures, there is evidence that Ru (0001) can support unusually high concentrations of oxygen at the surface[4,5]. In order to investigate the structure and stability of high coverage oxygen structures, we performed extensive density functional theory calculations for various O adlayers on Ru (0001). In particular, for the two ordered phases, (2×2)[6] and (2×1)[7], which form at room temperature under ultra high vacuum (UHV) conditions for coverages $\Theta = 1/4$ and $\Theta = 1/2$, respectively, as well as for an artificial (2×2)-3O adlayer with coverage $\Theta = 3/4$, and for several higher coverage (1×1)-O structures with $\Theta = 1$. Here, Θ is defined to be the ratio of the number of adsorbate atoms to the number of atoms in an ideal substrate layer. 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.

II. CALCULATION METHOD

We use density functional theory (DFT) and employ the generalized gradient approximation (GGA) of Perdew *et al.*[8] for the exchange-correlation functional. The surface is modelled using the supercell approach and we employ *ab initio*, fully separable pseudopotentials created by the scheme of Troullier and Martins[9], and a plane-wave basis set for expansion of the electronic wave functions. The calculations are performed using a (2×2) surface unit cell 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[10]. The energy cut-off is taken to be 40 Ry with three special **k**-points in the surface Brillouin zone[11]. The calculation scheme[12] affords simultaneous relaxation of the electrons and atoms using damped Newton 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. For the higher coverage (1×1)-O structures we use a larger energy cut-off of 60 Ry and 14 **k**-points in the irreducible part of the surface Brillouin zone of a (1×1) surface unit cell.

III. O ON RU (0001)

A. (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[6]. The binding energy of O (relative to a free O atom) in the hcp-hollow site is 5.55 eV and in the fcc-hollow site it is 5.12 eV (see Tab. I). We can compare this result with calculations for a single O adatom on an eighteen atom cluster model representing Ru (0001)[13], using an atom superposition and electron delocalization molecular orbital ASED-MO method. In this study it was found that the *fcc-hollow* site is the most

favorable with a binding energy of 5.6 eV. The hcp-hollow site was the next most favorable with a binding energy of 5.3 eV. Such cluster geometries are often regarded as representing the situation of an *isolated* adsorbate on an extended surface. Our calculated coverage dependence of the adsorption site of O, discussed below (see Fig. 4a), however, suggests that an isolated O adatom will occupy the hcp-hollow site.

The atomic geometry of (2×2)-O/Ru (0001) is displayed in Fig. 1. In Tab. II we compare the theoretically obtained structural parameters with those obtained by the LEED analysis[6]. For ease of comparison, we use the same notation as in the LEED study. We note that the theoretical lattice constant is 1.9 % larger than the experimental one. Rather than giving a detailed comparison of all the substrate relaxations, we simply refer to Tab. II, from which the high level of agreement with the LEED analysis can immediately be assessed. The theoretically obtained O-Ru bond length of 2.08 Å is slightly 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 %. Such a contraction is in contrast to many similar systems formed by adsorption of strongly electronegative species, where instead there is often an *expansion* induced by the adsorbate[1]. We find the top Ru-Ru interlayer spacing of Ru (0001) to be contracted by 2.5 % which is close to the LEED-determined value of 2.3 %[14]. The contraction of the top interlayer spacing of the clean surface is therefore not removed by oxygen adsorption at 1/4 monolayer.

B. (2×1)-O/Ru (0001)

At higher oxygen coverage, namely, $\Theta = 1/2$, a (2×2) LEED pattern is observed which corresponds to three rotated domains, each of (2×1) periodicity[7]. We performed calculations for O in the fcc- and hcp-hollow sites. The hcp-hollow site is again found to be energetically the most favorable with a binding energy of 5.28 eV; that for the fcc-hollow site is 5.00 eV (see Tab. I). The theoretical identification of the hcp-hollow site for O in the (2×1) structure is in accord with the LEED determination for the adsorption site[7].

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 from the center of the hcp-hollow site. In addition, complex O induced 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 Tab. III where they are compared with the results obtained from the LEED analysis[7]. Again, it can quickly be seen that quantitative agreement is achieved. We do note one

deviation however: The directions of the lateral displacement of atom D, $\Delta d_{\parallel}(D)$, have the opposite signs. 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 2.07 Å is very similar to that which we determined for the lower coverage (2×2) structure which was 2.08 Å. The value is again somewhat larger than that of 2.02 Å as obtained from the LEED 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.

C. (1×1)-O/Ru (0001)

We now investigate the structure and stability of (1×1)-O adlayers with coverage $\Theta = 1$. We performed calculations for O in the on-top, bridge, fcc-, and hcp-hollow sites. The obtained binding energies are collected in Tab. I. The hcp-hollow site is energetically preferred with a binding energy of 4.87 eV. The fcc-hollow site is the next most favorable having a binding energy of 4.81 eV. Table I also lists the binding energy differences for the adsorption sites tested, with respect to the binding energy of O in the respective hcp-hollow sites. The atomic geometry of (1×1)-O/Ru (0001) is shown in Fig. 3 and the O-Ru bond length and structural parameters are given in Tab. 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 %.

For comparison we also performed calculations for O in the hcp-hollow site using an energy cut-off of 40 Ry and three special **k**-points in the Brillouin zone[11]. As can be seen from Tab. IV, the resulting binding energy is 4.84 eV, i.e., only 0.03 eV less than the result of the more accurate calculation, and the resulting structural parameters differ by at most 0.02 Å.

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 ≈ 1.8 eV per atom) than that which the O atoms have in O_2. Under UHV conditions, however, the (2×1) phase is the terminal one. The reason that the (1×1) structure does not form under UHV conditions could be due to a kinetic hindering of the dissociation of O_2 induced by the (2×1) structure. 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[15]. 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 then it is probable that

the (1×1) phase will also be observed on Ru (0001) under UHV. This 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 metal surfaces can also support high O coverages.

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 common trend that atoms strongly chemisorbed on transition metal surfaces usually occupy the site that the next substrate layer would occupy.

In Fig. 4a the binding energy of O in the fcc- and hcp-hollow sites as a function of coverage is displayed. With increasing coverage the binding energy becomes less favorable which reflects a repulsive interaction between the adsorbates and implies that no island formation is expected to occur in the the coverage regime of $\Theta = 1/4$ to $\Theta = 1$. Figure 4a also shows that the difference in binding energy between the fcc- and hcp-hollow sites becomes less, as the coverage increases. As noted above, we also performed calculations for a structure with coverage $\Theta = 3/4$. In this structure we placed O atoms 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 %. The corresponding work function change as a function of coverage is shown in Fig. 4b. The experimental results of Surnev *et al.*[16] are included for comparison where good agreement between theory and experiment is obtained. The large increase in work function reflects the strong electronegative nature of O.

V. CONCLUSION

From our calculations we achieve quantitative agreement with previous structural determinations for (2×2)-O and (2×1)-O/Ru (0001) structures, with respect to the preferred adsorption site and the detailed atomic positions in the surface region. One minor difference is found for the (2×1) structure which would be worth a re-analysis of the LEED data. We predict that an O adlayer with a (1×1) periodicity and coverage $\Theta = 1$ should be able to form on Ru (0001), where the O atoms occupy hcp-hollow sites. For the coverage regime $\Theta = 1/4$ to $\Theta = 1$ there is no indication of island formation. The corresponding work function change agrees well with experiment.

[1] U. Starke, M. A. Van Hove, and G. A. Somorjai, Prog. in Surf. Sci. **46** (1994) 305.

[2] F. Besenbacher, J. K. Norskov, Prog. in Surf. Sci. **44** (1993) 5.

[3] K. C. Hui, R. H. Milne, K. A. R. Mitchell, W. T. Moore, and M. Y. Zhou, Solid State Commun. **56** (1985) 83.

[4] C. H. F. Peden and D. W. Goodman, J. Phys. Chem. **90** (1986) 1360.

[5] C. H. F. Peden, D. W. Goodman, M. D. Weisel, and F. M. Hoffmann, Surf. Sci. **253** (1991) 44.

[6] M. Lindroos, H. Pfnür, G. Held and D. Menzel, Surf. Sci. **222** (1989) 451.

[7] H. Pfnür, G. Held, M. Lindroos, and D. Menzel, Surf. Sci. **220** (1989) 43.

[8] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46** (1992) 6671.

[9] N. Troullier and J. L. Martins, Phys. Rev. B **43** (1993) 1991.

[10] J. Neugebauer and M. Scheffler, Phys. Rev. B **46** (1992) 16067.

[11] S. L. Cunningham, Phys. Rev. B **10** (1974) 4988.

[12] R. Stumpf and M. Scheffler, Computer Phys. Commun. **79** (1994) 447.

[13] A. B. Anderson and M. K. Awad, Surf. Sci. **183** (1987) 289.

[14] H. Over, H. Bludau, M. Skottke-Klein, G. Ertl, W. Moritz, and C. T. Campbell, Phys. Rev. B **45** (1992) 8638.

[15] S. L. Parrot, G. Praline, B. E. Koel, J. M. White, T. N. Taylor, J. Chem. Phys. **71** (1979) 3352.

[16] L. Surnev, G. Rangelov, and G. Bliznakov, Surf. Sci. **159** (1985) 299.

FIG. 1. Top view (a) and side view (b) of the atomic geometry of (2×2)-O/Ru (0001). The arrows indicate the direction of the displacements of the substrate atoms with respect to the bulk terminated 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 grey circles represent Ru atoms. Interlayer spacings are given in Ångstrom.

FIG. 2. Top view (a) and side view (b) of the atomic geometry of (2×1)-O/Ru (0001). The arrows 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 grey circles represent Ru atoms. Interlayer spacings are given in Ångstrom.

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. The arrows indicate the direction of the displacements of the substrate atoms with respect to the bulk terminated positions. Small dark grey circles represent oxygen atoms and large grey circles represent Ru atoms. Interlayer spacings are given in Ångstrom.

FIG. 4. (a) Binding energy of O on Ru (0001) for O in the fcc- (dashed line) and in the hcp-hollow site (continuous line). (b) Work function change as a function of coverage, Θ. The experimental results, shown as open circles, are from Ref.[16].

Sites tested		on-top	bridge	fcc-hollow	hcp-hollow
(2×2)				5.12	5.55
ΔE				0.43	0.00
(2×1)				5.00	5.28
ΔE				0.28	0.00
(1×1)		3.62	3.93	4.81	4.87
ΔE		1.25	0.94	0.06	0.00

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.

Structural parameters (Å)	(2×2)-O/Ru (0001)					
	O-Ru	$\Delta d_\parallel(A)$	$\Delta d_\parallel(D)$	Δd_z (A)	Δd_z (B)	Δd_z (C)
LEED	2.03	0.09	0.01	-0.05	-0.12	-0.08
DFT-GGA	2.08	0.07	0.01	-0.04	-0.11	-0.03

TABLE II. Structural parameters for (2×2)-O/Ru (0001) with O in the hcp-hollow site. $\Delta d_\parallel$ and Δd_z represent, respectively, lateral and vertical relaxations with respect to the bulk positions of the atoms indicated by the letters in parenthesis (see Fig. 1).

Structural parameters (Å)		(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		2.07	-0.06	0.01	-0.02	0.00
Structural parameters (Å)		$\Delta d_\parallel$(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		-0.03	-0.02	0.05	0.01	-0.02

TABLE III. Structural parameters for (2×1)-O/Ru (0001) with O in the hcp-hollow site. $\Delta d_\parallel$ and Δd_z represent, respectively, lateral and vertical relaxations with respect to the bulk positions of the atoms indicated by the letters in parenthesis (see Fig. 2).

Structural parameters (Å)	(1×1)-O/Ru (0001)					
	O-Ru	$d_{z,1}$	$d_{z,2}$	$d_{z,3}$	$d_{z,\text{bulk}}$	E_b (eV)
DFT-GGA (40 Ry)	2.04	1.28	2.27	2.19	2.19	4.84
DFT-GGA (60 Ry)	2.03	1.26	2.25	2.17	2.19	4.87

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

(a)

(b)

1.30
0.07
2.10
0.03
2.16
2.19

12

(a)

(b)

1.26
0.09
2.13
0.01
2.18
2.19

13

(a)

(b)

1.26

2.25

2.17

2.19

14