

HREEL spectra of various oxygen structures on Rh(110)

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High-resolution electron energy loss spectroscopy and low electron energy diffraction have been used to study ordered and disordered layers of oxygen adsorbed on the Rh(110) surface at different temperatures. It has been found that at temperatures of 90–120 K, low coverages of disordered atomic oxygen produce a single vibrational mode at 72 meV which is replaced by two losses at 45 and 63 meV when an ordered $(2 \times 1)p2mg$ monolayer is formed. Losses at 47 and 65 meV characterize the adsorbed oxygen in the $(2 \times 2)p2mg$, $(2 \times 3)p2mg$, and $c(2 \times 2n)$ structures produced at elevated temperatures, which involve reconstruction of the substrate. The changes in the vibrational spectra are explained in the framework of structural models where oxygen occupies different adsorption sites.

1. Introduction

The adsorption of oxygen on fcc (110) metal surfaces usually leads to the formation of ordered structures involving restructuring of the substrate surface. Recently, a number of studies of oxygen adsorption on Rh(110) have shown that depending on the preparation conditions a great variety of surface structures can be observed [1–6]. The only ordered structure observed after adsorption at 100–300 K is $(2 \times 1)p2mg$ with an oxygen coverage of one monolayer (ML). It has been suggested that the $(2 \times 1)p2mg$ structure is formed by zig-zag chains of oxygen located in threefold sites between two top and one second layer atoms. The reported sequence of ordered structures produced at elevated temperatures proceeds via $(2 \times 3)pg$, $(2 \times 2)p2mg$, $(2 \times 3)p2mg$, and $c(2 \times 2n)$ ($n=3, 4, 5$), corresponding to coverages of 0.25, 0.5, and 0.6–1 ML. Recent He diffraction and STM studies [5,6] confirmed the early suggestion [3,4] that these structures involve reconstruction of the Rh surface of the missing-row type. In the case of the $(2 \times 2)p2mg$ structure every second $[1\bar{1}0]$ row is missing, whereas in the case of the $c(2 \times 2n)$ structures every n th $[1\bar{1}0]$ row is missing. In order to satisfy the symmetry requirements it has been proposed that in the

$(2 \times 2)p2mg$ structure the oxygen atoms form zig-zag chains occupying a threefold coordinated site between two second layer and one third layer atoms along the missing row troughs. For the $c(2 \times 2n)$ structures the zig-zag chains are out-of-phase with oxygen located both in the (1×2) and (1×1) troughs between two top and one bottom Rh atoms [6]. Reduction with hydrogen or CO results in a (1×3) , (1×2) , and $(1 \times n)$ metastable surface which reverts to (1×1) at temperatures above 480 K [3,4]. However, it is not clear whether the metastable reconstructed surface is stabilized by some residue of subsurface oxygen as has been supposed in ref. [7].

In our previous paper on NO adsorption and dissociation on Rh(110) some high-resolution electron energy loss spectroscopy (HREELS) spectra observed for oxygen overlayers on Rh(110) produced at 100 and 300 K were reported [8]. The oxygen vibrational spectra showed a strong dependence on the adsorption temperature and oxygen coverage. We have suggested that the observed multi-loss oxygen spectra obtained at temperatures in the range 200–300 K indicate the coexistence of different oxygen species, involving an oxygen-induced reconstruction, subsurface penetration, and a surface oxide phase. In this Letter, we report the HREEL spectra

corresponding to the variety of ordered and disordered oxygen layers produced at low and elevated temperatures. The emphasis is on the determination of the local geometry of oxygen species on reconstructed and unreconstructed Rh(110) surfaces when ordered oxygen layers are formed.

2. Experimental

The experiments were performed in an UHV apparatus consisting of two chambers. The cleaning procedures, the characterization of the sample by low electron energy diffraction (LEED) and Auger spectroscopy, and the exposure to O₂, H₂, and CO were performed in the preparation chamber (base pressure 1×10^{-10} mbar). The base pressure in the chamber housing the ELS22 spectrometer was 4×10^{-11} mbar. The HREELS spectra were taken in the specular direction (incidence angle 60°) and 16° off-specular, with an energy resolution of 4–6 meV and a primary energy of 3 eV. The loss-peak intensities were normalized to the elastic peak intensity.

The Rh single crystal was oriented within 0.7° of the [110] direction. The cleaning procedure involved cycles of Ne⁺ bombardment, annealing to 1050 K in 2×10^{-8} mbar O₂, followed by annealing to 1100 K in 2×10^{-9} mbar H₂, until good surface order was detected by LEED, and no contaminants were visible in the Auger and HREEL spectra. The temperature was measured by using a chromel–alumel thermocouple spot-welded to the back of the sample. The oxygen layers were produced by exposures at different temperatures. The samples prepared at temperatures above 300 K were measured at room temperature, those prepared below 300 K were cooled with liquid nitrogen during the measurements. The coverage, θ , is estimated using the O(KLL)/Rh(MNN) Auger ratio measured after oxygen exposure, and is calibrated against the Auger ratio corresponding to one monolayer when a sharp $(2 \times 1) p2mg$ structure was observed [1–3].

3. Results and discussion

3.1. Oxygen adsorption at low temperature

Fig. 1 presents the HREEL spectra (specular mode) for oxygen layers produced by oxygen adsorption at 90–120 K. The only feature present in the spectrum after cleaning the sample (bottom curve) is a broad low frequency in the 15–25 meV range due to excitations of the Rh phonons. Initially, the adsorption of oxygen results in the appearance of a loss peak at 71 meV which shifts to 72.5 meV with increasing coverage. This loss peak dominates the spectrum up to a coverage of ≈ 0.3 ML where no extra spots in the LEED pattern are observed. In the 0–0.3 ML coverage range a loss at 55 meV and weak features in the 90–120 meV range can also be distinguished. In separate experiments with CO adsorption we found that the peak at 55 meV is due to Rh–C vibrational mode, which has a rather high cross section, and can be observed even with negligible

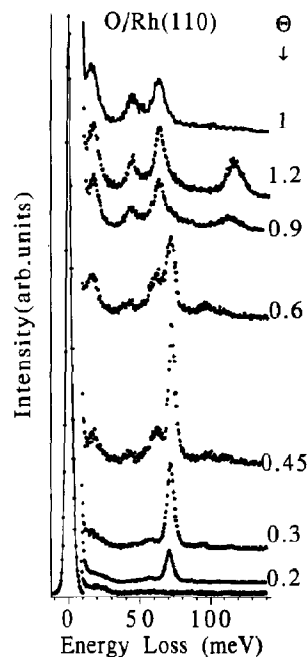


Fig. 1. HREEL spectra for increasing oxygen coverage on Rh(110) after adsorption at 90–120 K. The bottom spectrum represents the clean surface, the top spectrum a $(2 \times 1) p2mg$ monolayer obtained after removal of molecular oxygen by heating to 200 K. The scaling factor for all spectra is $\times 40$.

amounts of CO. With further increase of oxygen coverage, when the $(2 \times 1)p2mg$ structure starts to develop, new loss peaks at ≈ 42 and 62 meV emerge. They gain in intensity with increasing oxygen coverage, and shift to higher energy. The "low coverage" mode at 72 meV gradually decreases, and vanishes at saturation when the $(2 \times 1)p2mg$ structure is completely established. The ordering of the oxygen layer leads to an intensification of the loss feature associated with Rh phonons. The activation of the substrate phonons in the presence of ordered overlayers is due to induced perpendicular dipole activity as discussed in detail in ref. [9]. At high exposures a broad feature arises at ≈ 112 meV. It grows in intensity, and shifts to 117 meV at saturation. The frequency of this mode is within the range of the O–O stretching frequencies (80 – 135 meV) characteristic for chemisorbed molecular oxygen. In the previous studies on Rh(711) [10] and other transition metal surfaces [11–14] the features in the 128 – 133 meV range were related to oxygen present as a superoxo-species, and the features in the 103 – 108 meV range as peroxy-like species. Based on these data we tentatively assign the 117 meV mode to a peroxy-like species for which the frequency is affected by the presence of atomic oxygen. Slight annealing to 200 K to desorb molecular oxygen [3] removes the 117 meV loss peak (top curve), and causes a sharpening of the $(2 \times 1)p2mg$ pattern. Thus, the well-ordered $(2 \times 1)p2mg$ atomic oxygen layer is characterized by three relatively intense losses at 16 (Rh phonons), 45 , and 63 meV, and a weak broad structure in the 90 – 120 meV range.

Previous HREELS studies have shown that a Rh–O single stretch, ranging from 62 to 68 meV with coverage, characterizes oxygen occupying threefold sites on Rh(111) [15]. Oxygen on Rh(110) in the $(2 \times 1)p2mg$ structure has a vibrational frequency of 63 meV, which indicates that it does occupy the threefold sites in the troughs as we tentatively proposed previously [3]. The frequency characterizing the disordered layers at low coverage is higher (71 – 72.5 meV), and can be assigned to oxygen adsorbed in long-bridge sites. Comparison with the available data for other transition metals shows that this frequency is within the range of vibrational frequencies measured for both the threefold and twofold sites [9,16]. The coexistence of the 72 and 63 meV modes

at moderate coverage reflects a change in the local bonding configuration from bridging to threefold when the disorder to order transition occurs. This site conversion is required by the necessity to accommodate one monolayer of oxygen in the $(2 \times 1)p2mg$ structure as illustrated in fig. 2a. In fig. 2a oxygen is located between two top and one bottom atom as proposed previously in ref. [3]. The

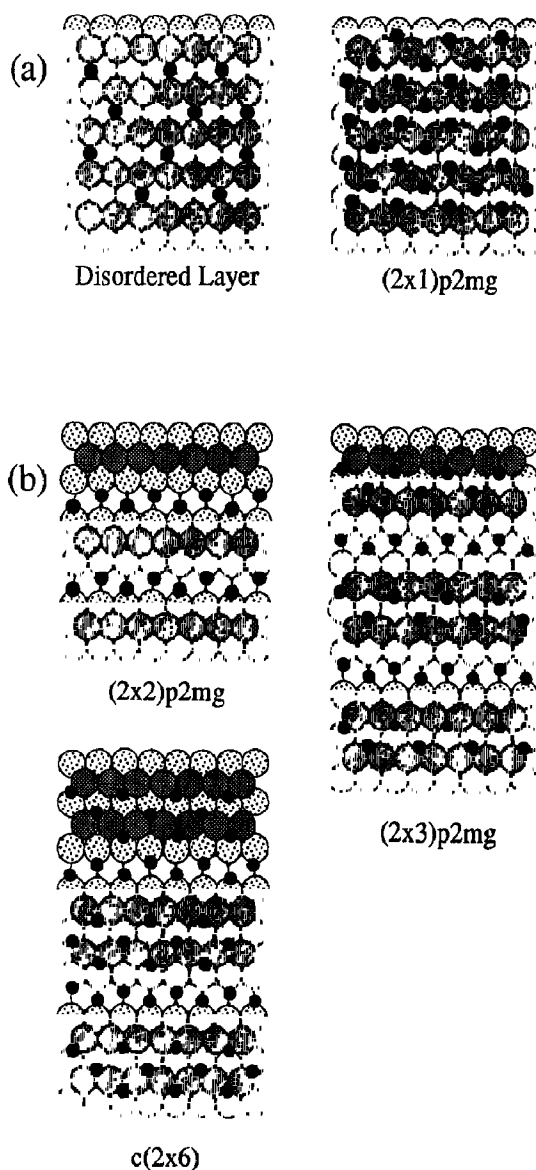


Fig. 2. Models of some of the structures observed after adsorption at low temperatures (a) and at elevated temperatures (b).

second possibility is oxygen located between one atom in the first and two atoms in the second Rh layers. However, both types of bonding can be described as threefold sites on a (111) facet so that they will be characterized by the same vibrational spectra. Since in this configuration the Rh–O bond is inclined against the surface normal, the vibration of oxygen along the [001] direction will induce a dynamical dipole moment with a component perpendicular to the surface, and can be detected in the specular direction. Using the equation for the frequencies of the perpendicular and parallel motions of an adatom in a threefold site, given in ref. [9], we calculated that, provided 63 meV is the symmetric mode, the corresponding parallel mode should be at 45 meV, which is in excellent agreement with the experimental data. In contrast, for oxygen in long-bridge sites the dynamical dipole moment associated with the vibrations parallel to the surface plane is totally screened. Indeed, at low coverage, when oxygen occupies these sites, only the normal Rh–O vibration at 72 meV is observed.

3.2. Ordered oxygen layers after adsorption at elevated temperatures

Fig. 3 shows HREELS spectra (specular and off-specular) for the (2×2) p2mg, (2×3) p2mg, $c(2 \times 6)$, and $c(2 \times 8)$ structures produced by ad-

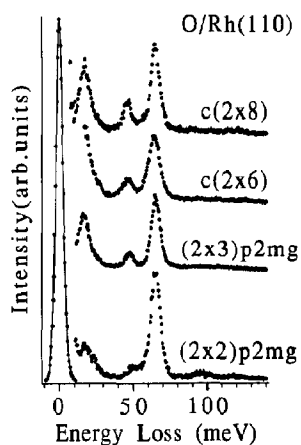


Fig. 3. Specular HREEL spectra of well-ordered oxygen layers produced at elevated temperatures (see text). The scaling factor for the spectra is $\times 60$.

sorption of oxygen at 570–620 K. To produce a sharp (2×2) p2mg structure the sample was flashed to 920 K after oxygen exposure. All specular spectra contain peaks at ≈ 16 and 65 meV, and weak broad features at ≈ 95 and 115–120 meV. The 65 meV peak dominates in all spectra but its intensity varies for the different structures (see table 1). As explained in section 3.1 the loss at 55 meV observed in the (2×2) p2mg spectrum is due to CO traces. With increasing oxygen coverage, when conversion from the (2×2) p2mg to (2×3) p2mg, and $c(2 \times 2n)$ structures occurs, the peak at ≈ 47 meV emerges, and gains in intensity. As a result the 47 to 65 meV intensity ratio, determined from a least-squares Gaussian fit of the spectra, increases from 0.2 for the (2×3) p2mg layer to about 0.4 for $c(2 \times 8)$ layer (see table 1). Obviously these two losses are growing at different rates with coverage, which indicates that the structural changes lead to different oxygen species. Here we would like to point out that this represents only a quantitative trend. The same conclusion can be drawn from the measurements performed in the off-specular direction, although the 47 to 65 meV intensity ratio is different here due to the different cross sections of the two modes in the impact scattering regime and the difference in the degree of order of the different structures. Similarly with the case of (2×1) p2mg, the ordered layers produced at elevated temperatures also activate the 16 meV loss peak related to the Rh collective excitations.

The HREELS data for oxygen layers obtained at elevated temperatures where oxygen induces a reconstruction of the substrate indicate that oxygen occupies threefold sites along the (1×2) and (1×1) troughs. Fig. 2b shows models for some of the ordered structures where the local geometry of the oxygen species is shown. These models are similar to the ones already proposed in ref. [6]. The difference is only in the local geometry of the oxygen adsorption site along the (1×2) troughs, and in the concentration of the oxygen atoms along the $[1\bar{1}0]$ rows. Considering the oxygen coverage of the (2×3) p2mg and $c(2 \times 2n)$ structures, we suggest that they can be best described when the oxygen local geometry along the (1×1) and (1×2) troughs is different. In the models in fig. 2b oxygen is located between the two top and one second Rh layer atoms along the (1×1) troughs (as in the (2×1) p2mg structure), and be-

Table 1

Intensity of the normal Rh–O modes, I_n , and intensity ratio of the parallel to normal Rh–O modes, I_p/I_n , measured for various structures on reconstructed and unreconstructed surfaces

LEED	Coverage		I_n	I_p/I_n	
	along (1×1)	along (1×2)		specular	off-specular
(2×2)p2mg	0	0.5	5.9	0	0.5
(2×3)p2mg	0.33	0.33	3.8	0.21	0.33
c(2×6)	0.50	0.33	4.6	0.32	0.74
c(2×8)	0.625	0.25	4.8	0.36	0.87
(2×1)p2mg	1.0	0	4.1	0.7	–

tween one second layer and two third layer atoms in the (1×2) troughs. As outlined in section 3.1, reverse ordering along the (1×1) and (1×2) troughs is also possible. In the (2×2)p2mg layer oxygen is located only in the (1×2) troughs, and produces only one perpendicular vibration at 65 meV. The suppression of the corresponding parallel mode is probably due to screening because of oxygen imbedded deep in the (1×2) troughs. Conversion to the (2×3)p2mg and c(2×2n) structures leads to population of the (1×1) troughs, where the bonding configuration of oxygen is similar to that of the (2×1)p2mg structure. As described in section 3.1, the growth of the 47 meV mode can be ascribed to the hindered translations of oxygen in the threefold sites in the (1×1) troughs. By reducing the concentration of the (1×2) troughs the contribution of the adatoms sitting in the threefold sites along the (1×1) troughs to the HREELS spectra increases, and leads to a rise of the 47 meV peak intensity. For reconstructed surfaces both the normal and parallel vibrational frequencies are ≈ 2 meV higher than that on a (1×1) surface. We suggest that this may be due to (i) the effect of the substrate structure on the motions of the Rh atoms in response to oxygen vibrations and/or (ii) the stronger Rh–O bonding on the reconstructed surfaces as reported in ref. [3]. The weak high-frequency features at ≈ 95 and 115–120 meV are within the range of vibrational frequencies for the diatomic Me–O molecule, and can be ascribed to oxygen adsorbed on top of a Rh atom. Another possibility is that they are due to an oxygen penetrated subsurface, which is also characterized by high-frequency losses in the 85–130 meV range [9,17,18], because oxygen is squeezed into a non-

equilibrium position. In support of the second suggestion is the fact that the high-frequency losses do not completely disappear after reduction of the surface oxygen by hydrogen when metastable (1×n) Rh surfaces are produced. This means that one cannot exclude the possibility that the reconstructed surfaces are stabilized by traces of subsurface oxygen. We would like to point out here that the reconstructed surfaces produced after reduction always contain a small amount of adsorbed CO with Rh–C, and C–O stretches at ≈ 55 meV and ≈ 245 meV, respectively.

3.3. Effect of annealing on the HREEL spectra of oxygen layers produced at 90–120 K

Fig. 4 illustrates the effect of heating to different temperatures for (2×1)p2mg and disordered layers. In the case of an ordered (2×1)p2mg monolayer (fig. 4a), heating to 300 K only removes the loss related to molecular oxygen, and improves the long-range order. After heating to 550 K the 45 to 63 meV intensity decreases, and a small shoulder reappears at ≈ 72 meV. In addition new rather intense loss features grow at ≈ 95 and 122 meV. The heating to 550 K also causes conversion from a well-ordered (2×1)p2mg to a poor c(2×10) structure with streaking in the [01] direction. Consequently, the HREEL spectrum obtained after heating to 550 K contains vibrations characterizing the intermediate stage of “nucleation and growth” of the c(2×10) islands, which involves substantial displacement of the substrate atoms. In this intermediate state a variety of non-equilibrium oxygen bonding configurations is possible. The latter give rise to intense high-fre-

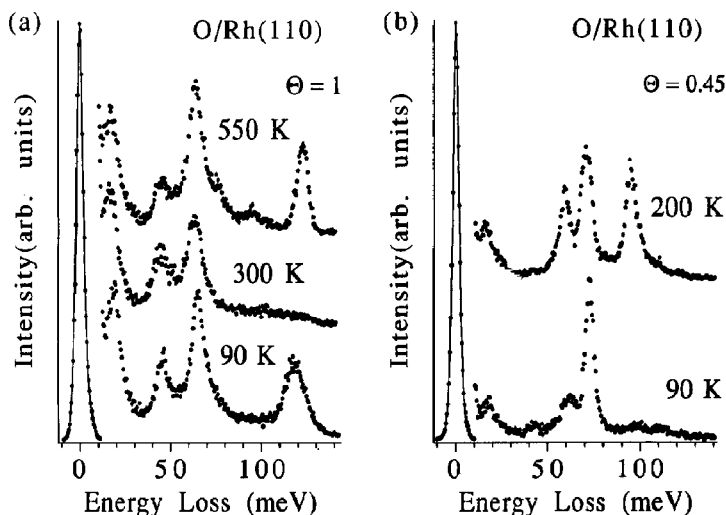


Fig. 4. Specular HREEL spectra measured after annealing of oxygen layers produced at 90 K for two oxygen coverages, the scaling factor is $\times 100$: (a) 1 ML; (b) 0.45 ML.

quency modes, which can be distinguished as weak features in the ordered layers. As noted in section 3.2, they can be ascribed to on-top and/or "subsurface" oxygen. The first possibility is an enhanced occupation of on-top sites because during the phase transition the concentration of small size islands and the density of antiphase boundaries increase substantially. One can speculate that oxygen in two single bonding configurations, e.g., on top of the $[1\bar{1}0]$ added rows and on top of the third row Rh atoms in the missing row, induces the 95 and 122 meV losses. The second possibility is that these losses are due to (i) oxygen atoms "buried" below the added $[1\bar{1}0]$ rows which nucleate and grow on the surface and (ii) oxygen incorporating a subsurface which destabilizes the substrate lattice and facilitates the displacement of Rh atoms. However, on the basis of the present data it is difficult to offer an unambiguous interpretation of the high-frequency loss features observed. Some support that they are more likely to be related to "subsurface" oxygen is the presence of weak features in the $(2\times 1)p2mg$ and $c(2\times 2n)$ spectra and the difficulty to remove them by reduction. Longbridge sites (72 meV) suggested for the disordered phase on a (1×1) surface are also occupied.

At lower oxygen coverage the structural transformation of the layers starts at lower temperatures. For 0.45 ML oxygen (fig. 4b) which shows a weak and

streaky $(2\times 1)p2mg$ structure, annealing to 200 K leads to substantial changes in the HREELS spectra with the appearance of an intense high-frequency mode, and a complicated LEED pattern with split $\frac{1}{2}$ extra spots and extra spots in $\frac{1}{5}$ position on both sides of the integer spots in the $[01]$ direction. Similar changes in the HREEL spectra with heating were also observed at a coverage less than 0.45 ML where, according to LEED, the oxygen layer is still disordered. It should be noted that at low coverages the growth of the high-frequency feature at ≈ 95 meV can be induced by very mild annealing to ≤ 200 K.

The observed effect of heating on the LEED patterns and HREEL spectra indicates that in the presence of oxygen a certain restructuring of the Rh(110) surface can be induced at temperatures as low as 200 K. However, complete conversion to the "missing-row" reconstructed surfaces requires high-temperature adsorption or annealing close to oxygen desorption temperatures of the $(2\times 2)p2mg$, $(2\times 3)p2mg$, and $c(2\times 2n)$ structures respectively [3-6]. The appearance of intensive losses in the high-frequency range after annealing might be taken as an indication that oxygen incorporation below the surface layer is an intermediate step towards a major reconstruction of the surface.

4. Conclusions

The HREEL spectra of the various oxygen structures on a Rh(110) surface obtained at different temperatures and coverages, clearly show that with increasing coverage and formation of ordered layers the bonding configuration of oxygen changes. In the disordered low-coverage phase, obtained at low temperature, oxygen is located in the long-bridge sites, and produces a single vibrational mode at 72 meV. Formation of an ordered $(2 \times 1)p2mg$ structure causes conversion of oxygen into threefold sites along the (1×1) troughs where the Rh–O bond is inclined with respect to the surface normal. The two modes characterizing this bonding configuration at 45 and 63 meV are due to vibrations of the oxygen adatoms parallel and normal to the surface. In the $(2 \times 2)p2mg$, $(2 \times 3)p2mg$, and $c(2 \times 2n)$ structures obtained at elevated temperatures, which involve reconstruction of the substrate, oxygen adatoms occupy threefold sites characterized by a normal mode at 65 meV, and a parallel mode at 47 meV. In the $(2 \times 2)p2mg$ structure, oxygen is located in the deep (1×2) troughs, and only the normal mode at 65 meV can be observed. The parallel mode at 47 meV becomes visible for the $(2 \times 3)p2mg$ and $c(2 \times 2n)$ structures, where oxygen starts to occupy the (1×1) troughs as well.

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