

When surface dynamics fakes symmetry: Oxygen on Rh(100) revisited

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Heating a long-range ordered adsorbate phase beyond its stability temperature does not necessarily result in a disordered phase; it can also break up into heavily fluctuating ordered domains. Temporal and/or spatial averaging over these fluctuations may give the impression of both a wrong periodicity and false symmetry elements such as nonexistent glide planes or rotational axes of incorrect order. This can happen in real space and reciprocal space, and also below liquid-nitrogen temperature, so that the true nature of the phase might remain undetected. We demonstrate this scenario at the catalytically active Rh(100) surface covered by $\frac{1}{2}$ monolayer of oxygen, using quantitative low-energy electron diffraction, variable-temperature scanning tunneling microscopy, and density functional theory. Using the example of CO adsorption, we show that local symmetry can have a decisive influence on the binding energy and thus the chemical reactivity.

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I. INTRODUCTION

The key for any understanding of catalytic reactions is the determination of active sites. These may either exist *a priori* at the catalyst's surface or develop during the reaction via surface restructuring induced by the reactants themselves. The decisive role of such reconstructions in determining surface chemistry and catalytic activity has been known for long [1] and hence a reliable structure determination of adsorbate phases on surfaces is paramount. One might assume that nowadays most structures at least of rather simple adsorbate systems on relevant model catalyst surfaces have been conclusively determined, since powerful computers enable a quantitative structural analysis both experimentally by diffraction methods [aided by real-space scanning tunneling microscopy (STM) imaging] and theoretically by efficient density functional theory (DFT) codes. Today's precision of theoretical modeling is sometimes considered even superior to experiment for revealing the true surface structure [2]. However, DFT often fails to predict the correct structural model without prior information and hence experimental techniques like quantitative low-energy electron diffraction (LEED) and STM are still urgently needed to elucidate the size and symmetry of the unit cell as well as the detailed atom positions.

In this study, we demonstrate that experimental methods may come up with incorrect answers when surface dynamics mask the true structure by giving the appearance of a false periodicity and/or local symmetry. This may readily occur when thermal activation creates a multitude of domain boundaries within a long-range ordered phase rather than random disorder. In such a case, LEED observes just a coherent superposition of snapshots from all domains within the coherence width. STM, on the other hand, measures a temporal average over domains fluctuating at timescales that are short compared to typical STM data acquisition times. Both these averages do not necessarily reflect the structural properties of any single domain. Thus, also the true nature and energetics of, e.g., available adsorption sites can be masked. We will demonstrate here that a Rh(100) surface covered by 0.5 ML oxygen atoms represents such a system. It is likely that more systems of that type exist that have remained undetected so far. The aim of this paper is to raise awareness of such a scenario.

Clean and adsorbate-covered Rh surfaces are popular model catalysts since rhodium is catalytically active in a variety of chemical reactions, e.g., inducing NO_x reduction [3] or alkane production [4]. In particular, for the CO oxidation reaction, recent work performed under realistic pressure conditions [5,6] shows that the oxygen-covered metallic surface is the active phase rather than the surface or bulk oxide. It was found that after ignition of the reaction at temperatures above 550 K, the surface is covered with about 0.5 monolayers (ML) of oxygen, while the CO content is below the detection limit [5]. At this oxygen coverage, the Rh(100) surface reconstructs and forms threefold-coordinated adsorption sites. Due to its presumed role in CO oxidation, the oxygen-induced reconstruction has attracted considerable experimental and theoretical interest [2,7–17]. The reconstructed phase is found

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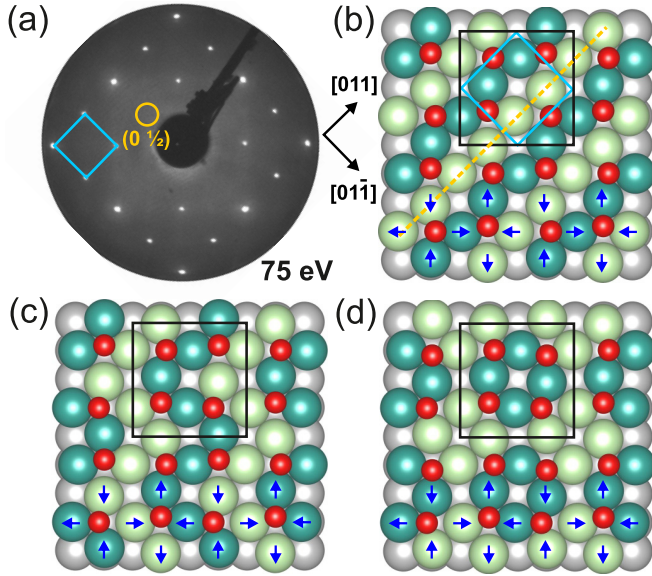


FIG. 1. (a) LEED pattern of the Rh(100) surface covered with 0.5 ML oxygen taken at 100 K. The pattern suggests a (2×2) unit cell (blue) with two orthogonal glide planes that cause extinction of the $(m + \frac{1}{2}, 0)$ and $(0, n + \frac{1}{2})$ beams (the position of one is marked by a yellow circle). (b) Top view of the (2×2) pg structure proposed by Baraldi *et al.* [12]. This model possesses one glide plane only (yellow). (c), (d) Two proposed variants of the model [panel (b)] that enlarge the unit cell to a Rh(100)- $(2\sqrt{2} \times 2\sqrt{2})R45^\circ-4O$ structure (black). The structures are obtained from panel (b) by letting the lower right [panel (c)] and also the upper right [panel (d)] oxygen atoms of the “ $2\sqrt{2}$ ” cell hop to an equivalent site of the reconstructed Rh(100) surface. In all models, half of the Rh atoms in the top layer are singly coordinated with oxygen (colored light green) and the other half are doubly coordinated (dark green). The arrows in panels (b)–(d) indicate the lateral relaxation pattern of the top-layer Rh atoms.

to be stable up to about 800 K [9] and should therefore represent the active phase in the CO oxidation reaction [5]. It shows a (2×2) LEED pattern with systematic extinction of half-order spots along the two k axes [Fig. 1(a)], indicating two perpendicular glide planes within the structure. The currently favored structural model based on the work of Alfé *et al.* (DFT [11]), Baraldi *et al.* (LEED [12]), and Norris *et al.* (x-ray diffraction [14]) is depicted in Fig. 1(b): The first-layer Rh atoms form the characteristic “clock” reconstruction creating pseudo-threefold hollow adsorption sites for oxygen atoms.

However, structural parameters obtained by different methods do not coincide within the mutual error margins. Even more severe is the fact that the model has one glide plane only (pg symmetry) and the incoherent superposition of the expected 90° rotational domains would not lead to the extinction of the $(m + \frac{1}{2}, 0)$ and $(0, n + \frac{1}{2})$ LEED beams ($m, n \in \mathbb{Z}$) as observed in experiment.

In the light of these discrepancies and noting the only mediocre fit quality of the LEED study mentioned ($R_{\text{Pendry}} = 0.28$) [12], we decided to revisit this system in a concerted effort applying LEED intensity analysis [LEED- $I(V)$], variable-temperature STM, and DFT.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

All LEED- $I(V)$ data acquisition, the structural analyses as well as DFT calculations and short-range order simulations were performed in Erlangen. All low-temperature STM data were taken in Vienna. A more detailed description of the procedures will be given in a forthcoming publication [18].

A. Experimental details

All experiments were carried out in ultrahigh vacuum (UHV). The Rh(100) surface was prepared by several cleaning cycles, each consisting of subsequent Ar^+ bombardment, annealing at 870 K in 1×10^{-6} mbar O_2 and a final flash to 1090 K in UHV.

The 0.5 ML oxygen phase was prepared by dosing the clean Rh(100) surface with molecular oxygen either at room temperature until no further dissociation takes place (at about 9×10^{-7} mbar s) or, alternatively, at a temperature of 870 K and pressure of 1×10^{-6} mbar O_2 , which is beyond the stability limit of the next denser (3×1) -2O phase [19] and thus also self-limiting. The latter produced an extremely well-ordered surface, free of any contamination, as proven by our low-temperature STM analysis. The LEED data of the two preparation methods did not show any noticeable differences.

The UHV chamber in Erlangen (base pressure $\approx 2 \times 10^{-11}$ mbar) housing an ERLEED optics and a room-temperature beetle-type STM is described in Ref. [19]. In this system, the sample could be heated rapidly to temperatures up to 1400 K by electron bombardment from the rear and cooled to about 100 K by direct contact to a liquid-nitrogen reservoir within minutes. The temperature was measured by a K-type thermocouple spot-welded directly onto the rim of the crystal. The sample holder allowed for independent sample rotation around two orthogonal axes lying both within the surface plane for precise normal incidence of the electron beam during LEED- $I(V)$ data acquisition (accuracy $\approx 0.1^\circ$). To minimize both the influence of residual gas adsorption and the thermal diffuse scattering background, data acquisition was started immediately after the temperature reached 120 K in the cool-down process. The LEED pattern was recorded by a CCD camera between 40 and 600 eV in 0.5 eV steps and stored on a computer for later off-line evaluation. The $I(V)$ spectra were averaged between symmetrically equivalent beams, slightly smoothed for noise removal, and normalized by the simultaneously recorded primary beam current. This resulted in a database for the LEED analysis of $\Delta E \approx 7000$ eV.

The experiments in Vienna were also performed in a two-chamber UHV system consisting of a similarly equipped preparation chamber (base pressure 7×10^{-11} mbar) and an adjacent analysis chamber (base pressure 5×10^{-12} mbar). The analysis chamber hosts a low-temperature STM (Omicron LT-STM) operating at 79 and 6 K using electrochemically etched W tips. In this system, annealing temperatures were measured by a thermocouple on the nontransferable part of the sample holder, which leads to estimated errors of ≈ 50 K at the annealing temperature.

B. Computational details

Full-dynamically calculated model intensities as well the optimization of model parameters by means of *tensor LEED* were performed using the *ViPERLEED* package [20] implementing the phase shift program *EASiSSS* [21] and the *TENSORLEED* program package [22]. For quantification of the agreement between experimental and theoretical spectra, the Pendry *R* factor *R* [23] was used.

In the LEED analysis, we varied all geometrical parameters of oxygen and rhodium atoms of the first two layers as far as allowed by symmetry, as well as interlayer distances of the third and fourth Rh layers. Additionally, vibrational amplitudes were varied for the oxygen atoms and the top-layer Rh atoms as well as a constant shift of the experimental energies to account for the work function of the cathode and the unknown reference value of the calculated inner potential curve [21]. This resulted in a total of $P = 23$ free parameters (17 structural and 6 nonstructural), which have been adjusted. The fit can be regarded as highly reliable because of the large $I(V)$ database ΔE used [redundancy factor $\rho = \Delta E / (4V_{0i}P) \approx 15.7$, with the optical potential V_{0i}].

All DFT calculations were performed using VASP [24], employing the general gradient approximation of Perdew, Burke and Ernzerhof (PBE) [25] and its refinement PBEsol [26]. For comparison, calculations were also performed with the optB86b vdW functional of Klimeš *et al.* [27]. Nine-layer Rh(100)-(2√2×2√2)R45° slabs with all atoms left free to relax and a 15 Å vacuum gap were set up. Oxygen atoms were positioned on one surface of the slab only. The calculations were performed with an energy cutoff of 550 eV employing an automatically generated 10×10×1 Monkhorst *k*-point mesh (50 irreducible *k* points). Convergence tests revealed that at those settings energies are reliable to below 5 meV. For the climbing image nudged elastic band (CI-NEB) method, we used the implementation of the Henkelman group [28,29]. For presentation and comparison with LEED results, all calculated values were scaled by the ratio of the bulk Rh lattice constant from experiment (3.80 Å) and that obtained from bulk calculations of Rh employing the respective functionals. Lattice parameters: PBE, 3.83 Å (same as Ref. [30]); PBEsol, 3.78 Å; and optB86b, 3.80 Å.

III. RESULTS AND DISCUSSION

When we tested our LEED data against the proposed (2×2) model of Fig. 1(b), we surprisingly arrived at an excellent Pendry *R* factor of $R = 0.106$ with essentially the same model parameter values as given by Baraldi *et al.* [12]. This leads us to believe that some technical error has occurred in that previous analysis. However, we cannot corroborate their statement that the half-order spots along the *k*-space axes resulting for this model structure are too weak to be detected in experiment; in contrast, their predicted intensity is clearly sufficient for observation (for details, see Ref. [18]). Therefore, even the excellent fit quality of the LEED analysis achieved here is not able to eliminate the discrepancies described in the Introduction.

How is it possible that a structural model matches the quantitative diffraction data almost perfectly, yet is still in-

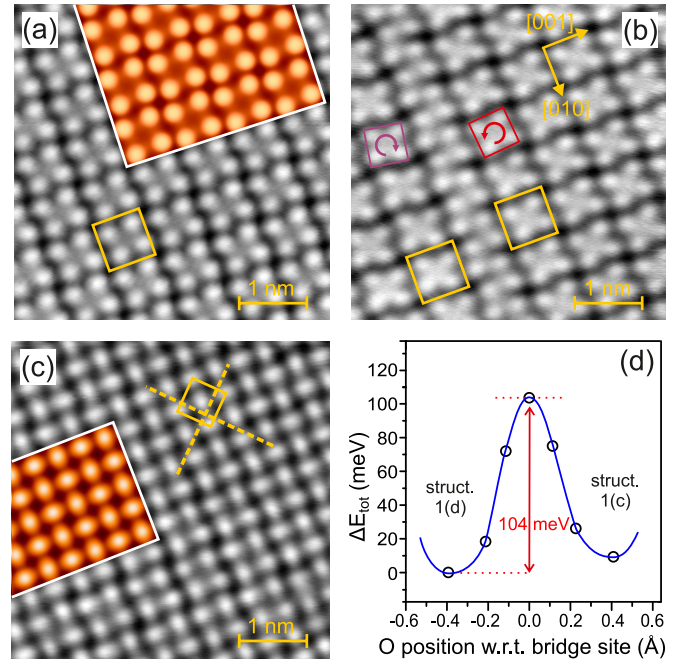


FIG. 2. STM images (3.6 nm×3.6 nm; ±20 mV; 1.5 nA) of the 0.5 ML oxygen phase on Rh(100) taken at 6 K [panels (a) and (b)] and 78 K [panel (c)] with the apparent translational symmetry indicated by yellow squares. (a) Single domain of the 2√2 phase together with the STM simulation (colored, framed by a white line) of the model in Fig. 1(d). (b) A domain boundary between two mirror domains, where oxygen atoms are arranged according to Fig. 1(c). (c) Apparent (2×2) periodicity with two glide planes (dashed yellow lines) with some indications of a 2√2-like region in the lower part. Overlaid (framed by a white line) is an STM simulation for quasimultaneous site occupation. (d) DFT calculation of the energy barrier between the two relaxed structures of Figs. 1(c) and 1(d) that differ in the position of one oxygen atom. The blue line is a guide to the eye.

compatible with the symmetry observed in diffraction? The good correspondence between experimental and theoretically predicted intensities excludes significant variations of local atomic positions of both Rh and O atoms without heavily deteriorating the fit. The only way out is to keep the Rh clockwork reconstruction and find models with a different spatial arrangement of oxygen atoms among the threefold hollow sites, which exist on either side of the long-bridge positions. This is in line with previous suggestions that this system may be dynamic with local disorder except at very low temperatures [12,13]. Note that such an *ordered* model cannot be defined in the (2×2) cell since any site switch of one of the two oxygen atoms in the cell always results in a symmetry-equivalent cell. The next larger cell where two further nonequivalent configurations can be found is a (2√2×2√2)R45° cell (hereinafter referred to as “2√2” for short), depicted in Figs. 1(c) and 1(d).

Although this approach at first glance contradicts the symmetry and size of the unit cell as measured by LEED [Fig. 1(a)], it is supported by low temperature STM images of the system at $T = 6$ K. Figures 2(a) and 2(b) clearly show the presence of a 2√2 unit cell (yellow squares). We can identify

TABLE I. Calculated total-energy difference ΔE in meV per $2\sqrt{2}$ cell of models Figs. 1(b) and 1(c) with respect to the lowest-energy configuration of model Fig. 1(d) for various functionals.

Model	PBE ΔE (meV)	PBEsol ΔE (meV)	optB86b ΔE (meV)
Figure 1(b)	+14	+28	+23
Figure 1(c)	+3	+9	+8
Figure 1(d)	0	0	0

this phase as corresponding to the model of Fig. 1(d) via the excellent agreement with a simulated STM image (employing the Tersoff-Hamann approximation [31]), which is overlaid in Fig. 2(a). This also proves that the bright protrusions imaged in STM are the oxygen atoms within the structure. Due to their off-center position at threefold-coordinated sites of the substrate's reconstruction, the quartets of oxygen atoms are slightly rotated against the crystallographic main axes, either clockwise or anticlockwise, so that two mirror domains are possible. Figure 2(b) displays the boundary between such two domains, which consists of a well-defined stripe, where every four oxygen atoms are arranged in a trapezoidlike configuration. This arrangement is the motif in the model of Fig. 1(c). In contrast, a simple diagonal zig-zag arrangement of oxygen atoms, which would be characteristic of the conventional (2×2) model, cannot be found anywhere on the surface.

These experimental findings can be rationalized by comparing the total energies of the structural models of Figs. 1(b)–1(d) resulting from our DFT calculations (cf. Table I). Independent of the functional chosen for the calculation, model (d) always turns out to be the configuration with the lowest total energy (set to zero), closely followed by model (c), which is only 3–9 meV less favorable per $2\sqrt{2}$ cell. In contrast, the (2×2) model (b) is about 20 meV higher in energy. This means that the observed $2\sqrt{2}$ configuration is indeed the ground-state structure of the 0.5 ML O/Rh(100) system.

With respect to the local structure, all three models are rather similar. Rh atoms bound to two oxygen atoms always behave as if being larger in size compared to single-coordinated ones: They buckle out of the surface by ≈ 0.1 Å and whenever possible they assume larger distances from each other. The three models only differ in the way in which these two classes of structurally distinct Rh atoms are arranged within the topmost layer. In Fig. 1(b) they form linear chains, whereas in Fig. 1(c) they zig-zag across the surface and in Fig. 1(d) they form squares. Hence, it appears reasonable to correlate the energy differences with their ability to relax, considering the different effective atomic sizes of Rh atoms. This is certainly unfavorable in the case of the (2×2) structure with its almost linear arrangement of atoms of the same type and best for the squares that can alternately expand and contract in a checkerboard pattern.

In STM, the appearance of this phase changes significantly when the temperature is increased to 78 K [Fig. 2(c)]. Over wide areas, the oxygen atoms appear no longer as tetramers but as equally spaced, though with an elongated shape, alternately stretched along the [010] and [001] directions. So, in STM we observe a (2×2) mesh with p4gm symmetry. Since

the alternating elongation of STM protrusions just coincides with the directions in which neighboring threefold adsorption sites are aligned, the obvious interpretation of this finding is due to a rapidly fluctuating occupation of adjacent sites. For that, the oxygen atoms must change position in between these sites with a rate much faster than the scan speed of the STM tip.

This picture is supported by a DFT-based estimate of the diffusion barrier that determines the hopping rate of one single O atom within the $2\sqrt{2}$ cell, which switches the structure from model Fig. 1(d) to Fig. 1(c). To that end, we employed the CI-NEB method [28]. The resulting minimum-energy path is shown in Fig. 2(d), where the barrier is ≈ 100 meV (PBEsol). Using an attempt frequency derived from a harmonic approximation to the energetic minima yields a rate of thermally activated hops on the order of megahertz at 78 K. Thus, they are indeed much faster than the image acquisition (0.3 ms/pixel). As a consequence, this STM image is a *time average* of the surface configurations. The elongated atoms in Fig. 2(c) correspond exactly to the superposition of images of an oxygen atom taken at 6 K on either side of the short-bridge barrier, which is visualized in a corresponding STM simulation overlaid in Fig. 2(c).

From the STM image, we cannot infer whether the oxygen atoms completely loose or locally retain their lateral order, i.e., we cannot decide whether they hop independent of each other or coherently, i.e., their hops are associated with domain boundaries, letting them fluctuate across the surface. This, however, is possible by a quantitative LEED intensity analysis. Here, the scattering of electrons is instantaneous on the timescale of the hopping motion of the oxygen atoms so that the electrons just “see” snapshots of the adsorbate distribution. Moreover, the beam intensities are generated via multiple scattering processes on a spatial range of the electron's attenuation length, which is on the order of 10 Å, and thus are very sensitive to the local order. We therefore fitted two alternative models to our experimental LEED- $I(V)$ data taken at 100 K: An ordered $2\sqrt{2}$ according to Fig. 1(d) and a (2×2) with both quasithreefold oxygen adsorption sites being half-filled and the scattering between these two is neglected (to mimic statistical site occupation). For the latter model we achieve a best-fit R factor of $R = 0.096$, not much better than the value of $R = 0.106$ obtained by us for the previous (2×2) model. In contrast, the $2\sqrt{2}$ model resulted in an ultralow R factor of $R = 0.073$ and, in combination with the large data base used for the analysis, a very low variance [23] of $\text{var}(R) = 0.005$. We can therefore rule out the other structural models with high statistical significance. A detailed discussion of the resulting best-fit structure and error margins for the fitted parameters is given elsewhere [18]; a structure file of the LEED best-fit is supplied as Supplemental Material [32].

At this point, where the presence of $2\sqrt{2}$ domains at the surface is evidenced also at temperatures around 100 K, the reader might wonder why there are no characteristic quarter-order spots visible in the LEED pattern. Indeed, also our model calculations predict a sufficiently high intensity level for these spots to be easily detected. Their extinction in experiment can be explained by *coherent* scattering effects as follows: We know already that the domain boundaries between mirror domains consist of single cells of the structure

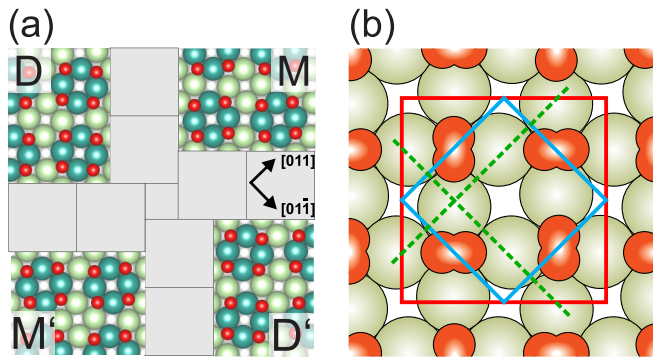


FIG. 3. (a) At 100 K, LEED will detect a momentary domain configuration as schematically shown. The gray $2\sqrt{2}$ areas are filled by the domain boundary structure [Fig. 1(c)]. The coherent superposition of the domains in panel (a) will produce a LEED pattern corresponding to the effective surface structure displayed in panel (b). This structure has a (2×2) unit cell (blue square) with two orthogonal glide planes (green dashed lines).

displayed in Fig. 1(c) [cf. Fig. 2(b)], which cost only a few meV to create (Table I). Hence, at 78 K they must be excited in large numbers. The structure decays into a multitude of nanodomains within the coherence area of the LEED experiment (typically 200 Å in diameter). We also see from Fig. 2(b) that mirror domains are shifted by half a $2\sqrt{2}$ unit vector relative to each other. Due to the fourfold symmetry of the structure, we obtain domain boundaries in two perpendicular directions producing a total of four differently aligned domains D, D', M, and M' shown in Fig. 3(a). D' and M' are identical to D and M, but laterally shifted by half a cell diagonal; i.e., they are perfect antiphase domains. Since the underlying (2×2) clock reconstruction of the substrate is monodomain over very large distances, all $2\sqrt{2}$ domains of the same type are exactly in phase and thus would produce sharp spots on their own like a continuous grid with a fractional site occupancy. Additionally, we have to regard the *interference* of scattered waves from all four domains. In particular, the quarter-order beams produced by the domains D and D' (or M and M') are scattered strictly antiphase and because of equal statistical weights this leads to extinction via destructive interference. The whole scenario can be modeled by a projection of all fractional scatterers (each with the respective lateral shift) on to the same unit cell as shown in Fig. 3(b). It clearly exhibits a higher symmetry than each of the single domains. This configuration can be described by a smaller (2×2) unit mesh and it also possesses two perpendicular glide planes indicated by dashed lines (a mathematical proof is given elsewhere [18])—exactly what is observed in the LEED pattern. In fact, with extreme contrast enhancement we find very weak and diffuse quarter-order spots originating from short-range order effects indicating an average nanodomain size of about 18 Å at 100 K. (For details, see Ref. [18].)

Finally, we want to emphasize that the knowledge about the correct surface structure is not an end in itself, but it is important for a microscopic understanding of surface-related processes like adsorption or catalytic reactions. Considering, e.g., coadsorption of a CO molecule, then the formerly accepted (2×2) pg model solely offers one type of fourfold-

TABLE II. Calculated adsorption energy differences ΔE_{ad} per $2\sqrt{2}$ cell for a CO molecule placed on different fourfold hollow sites (h) or bridge sites (b) of models displayed in Figs. 1(b) and 1(d). The sites differ by the O-coordination of involved Rh atoms (solely one- or twofold, or one- and twofold (1,2) mixed). (*) Lateral positions of topmost Rh atoms kept fixed. (**) Topmost Rh atoms relax into an unreconstructed arrangement.

Structure	O-coord. of Rh	O adsorption site	ΔE_{ad} (meV)
(2×2) h	1, 2-mixed	Moved toward bridge	+172
$2\sqrt{2}$ h	Onefold	Fourfold hollow	0
	1, 2-mixed	Fixed at fourfold hollow	+701
	Twofold	Fourfold hollow	+1063
$2\sqrt{2}$ b	1, 2-mixed	Moved to bridge*	+175
	1, 2-mixed	Moved to bridge**	+2

coordinated hollow sites, where two Rh atoms are singly and two are double coordinated to oxygen, cf. Fig. 1(b). DFT predicts that a CO molecule adsorbing on such a site would strongly distort the structure and eventually relax toward a bridge site. In contrast, the true $2\sqrt{2}$ structure additionally exhibits two further types of fourfold hollow sites, one with exclusively single and one with double O-coordinated Rh atoms [cf. Fig. 1(d)]. The former are the preferred adsorption sites. This may come as a surprise, since CO occupies top sites on the pure Rh(100) surface and, at higher coverage, also bridge sites [33], but never hollow sites (0.1–0.2 eV less favorable). On the oxygen-precovered surface, however, the repulsion of the neighboring oxygen atoms predominates (reducing the binding energy by approximately 0.8 eV), so that the singly coordinated hollow site, which maximizes the distance from the oxygen atoms, becomes the most favorable. Our DFT calculations also found another energetically almost degenerate configuration with a bridge-bound CO and, correspondingly, an O atom that is also displaced to an opposite bridge position. However, this structure is associated with a lifting of the Rh clock reconstruction (yielding 175 meV in the presence of bridge-bonded CO), which is not possible in reality due to stabilization by the neighboring cells.

The calculated adsorption energies differ by more than 1 eV among these sites (see Table II). In particular, the all-single O-coordinated hollow site [square of light-colored atoms in Fig. 1(d)] is found to be by 0.17 eV more favorable than the mixed O-coordinated site offered by the (2×2) pg phase. In practice, the CO oxidation reaction in the current system takes place at much higher temperatures, at which the oxygen is (practically) evenly distributed between the two adjacent threefold hollow sites meaning that there is no longer any order-dependent availability of different sites. However, the large differences of adsorption energies (cf. Table II) will cause CO to restore the $2\sqrt{2}$ structure, at least locally, already during the adsorption process. This means that the actual initial configuration in the oxidation reaction is a CO molecule in a fourfold-hollow site formed by singly oxygen-coordinated Rh atoms and not, as would be concluded from the previous (2×2) pg model, a bridge-bound CO with a severely distorted Rh reconstruction below. Consequently, any attempt to calculate adsorption energies or reaction barriers and pathways on the basis of the wrong structural model would also lead to

significantly incorrect results. Therefore, this system serves as a prime example of how strongly local ordering effects can influence the chemical properties of a system. There is no microscopic understanding of the catalytic action of such a system without the unambiguous identification of available adsorption sites.

IV. CONCLUSIONS

We have identified the true ground-state structure of the 0.5 ML oxygen phase on Rh(100), which is effectively hidden from recognition by standard structure-sensitive methods like qualitative LEED or STM. This is because already at 100 K this phase breaks down into an ensemble of rapidly fluctuating nanodomains. The superposition of their contributions to any method fakes both the apparent periodicity and local symmetry and, hence, inevitably leads to wrong model structures. Consequently, also other physical or chemical properties of the surface like adsorption sites or reaction barriers derived from the wrong structure model will be inaccurate or invalid. The prerequisites for such a scenario are

a low formation energy for domain boundaries and a high hopping rate of adatoms at the temperature of investigation. As these requirements are fulfilled in a large number of systems, we expect more cases of this kind, which still await discovery.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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