The influence of incommensurability on the long-range periodicity of the Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-PdO(101)

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Abstract

The structural model of the ($\sqrt{5} \times \sqrt{5}$)R27°-PdO(101) surface oxide grown on Pd(100) has been proposed and refined by a number of authors over more than a decade. In the current contribution we discuss the long-range periodicity of this structure arising along one of the crystallographic directions due to its incommensurability with the substrate. Analyzing the results of surface sensitive diffraction studies, we determined a slight distortion of the previously reported perfect ($\sqrt{5} \times \sqrt{5}$)R27° surface oxide unit cell. Considering it, we were able to achieve both qualitatively and quantitatively better fit to the experimental diffraction data than it was possible for the perfect structure. Further, taking into account the experimentally obtained scanning tunneling microscopy data and closely examining high-resolution patterns recorded by means of high-energy surface X-ray diffraction, we developed a qualitative structural model based on a larger non-orthogonal surface unit cell to shed more light on the long-range order of the PdO(101) surface oxide. The model comprises a shift of the atoms of the PdO perpendicularly to the direction of the incommensurability to correct for it. This structural model reproduces the fine details of the high-resolution

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diffraction patterns and qualitatively explains the periodic stripes of structural distortion observed in the images recorded by a scanning tunneling microscope.

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1. Introduction

The chemical and physical properties of late transition metals have been extensively studied due to the wide range of their applications including heterogeneous catalysis as a prominent example [1]. Pd, in particular, is one of
5 well known materials for oxidation catalysis employed in, e.g. CH₄ combustion [2, 3, 4] or CO oxidation [5]. An everyday example is automotive catalytic converters, where Pd acts as a catalytically active material dispersed on a porous support in the form of nanoparticles to maximize the surface area [6].

In order to understand in detail the catalytic performance of existing cata-
10 lysts and to design novel approaches in the field of catalysis, it is important to investigate the surface structure and its interaction with the reactants on the atomic scale. A common way to approach this problem is to use single crystals as model systems [7]. In this way, experimental difficulties connected with the limited access to the surface of nanoparticles in a real industrial catalytic
15 converter can be avoided.

The interaction of oxygen atoms with Pd single crystal surfaces play a crucial role in catalytic reactions, which involve oxygen as one of the reactants. In the above mentioned reactions of CO oxidation and CH₄ combustion, the growth of PdO on the surface has been reported repeatedly when the sample
20 is catalytically active [8]. In particular, extensive studies of a Pd(100) single crystal surface acting as a model catalyst in the process of CO oxidation under semirealistic conditions showed an increase in the reaction rate simultaneously with the formation of a Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-PdO(101) superstructure or an epitaxial PdO(101) film on the surface suggesting a high reactivity of this

25 phase [9, 10, 11, 12]. A high reactivity of the PdO(101) surface has also been reported for thicker epitaxial PdO(101) films on Pd(111) under Ultra High Vacuum (UHV) conditions [13]. The catalytic activity can be explained by the presence of coordinatively unsaturated Pd atoms in the structure, highlighting the importance of accurate structural determinations for the understanding of
 30 structure-function relationships.

The structure of a Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-PdO(101) surface oxide grown in pure oxygen has previously been studied by Low-Energy Electron Diffraction (LEED), Density Functional Theory (DFT) calculations, Scanning Tunneling Microscopy (STM) and High-Resolution Core Level Spectroscopy (HRCLS) and
 35 the atomic structural model was proposed [14, 15]. Later we have studied the same structure in detail by High-Energy Surface X-Ray Diffraction (HESXRD) *in situ* during CO oxidation [16]. By fitting the diffraction data we have retrieved the atomic coordinates of a Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-PdO(101) surface oxide under reaction conditions, which turned out to be similar to the structure
 40 observed in pure oxygen. Some details of the long-range structure of the oxide observed in the diffraction experiments were, however, omitted in the previous publications with the intention to discuss them in a separate work.

In the current contribution we have investigated in detail the long-range structure of a Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-PdO(101) surface oxide influenced by its
 45 incommensurability with the substrate along the $[01\bar{1}]$ crystallographic direction. For this purpose we use the data obtained by Surface X-Ray diffraction (SXRD), HESXRD, STM and LEED under UHV conditions as well as during CO oxidation.

2. Experimental details

50 Before all measurements, the surface of a Pd(100) single crystal was sputtered by cycles of Ar⁺ bombardment at 1.5 keV energy and 2×10^{-5} mbar pressure of Ar gas with subsequent annealing of the sample at 1000 K *in vacuo*. The surface was considered to be clean when the corresponding diffraction patterns

indicated sharp features characteristic for the (100)-oriented metallic surface
55 (see Figure 1a for LEED and Figure 3a for HESXRD).

The LEED and the STM studies were performed in the same experimental setup located at the Division of Synchrotron Radiation Research at Lund University, Lund, Sweden. A standard Omicron STM1 microscope and a LEED instrument are mounted in a UHV chamber with the base pressure of about
60 5×10^{-11} mbar. The STM images were recorded using a tungsten tip in the constant current mode with post processing including background subtraction and brightness/contrast enhancement.

The SXRD measurements reported in the present work were performed at the Max Planck beamline at Angströmquelle Karlsruhe (ANKA) [17]. The
65 available photon beam had a typical flux on the order of $3 \cdot 10^{10}$ photons/s and the energy of 10 keV with the size of the cross-section of about 0.35×0.35 mm². The sample in a XRD compatible UHV chamber equipped with gas inlet, heating stage and sputter gun was mounted on a Z-axis surface diffractometer [18] and the diffracted radiation was recorded by a NaI point scintillator detector.

70 The HESXRD experiments were carried out at the Physics Hutch of the P07 beamline at PETRA III at Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany [19]. The photon energy of 85 keV was employed for the measurements and the incoming beam focused to the size of 3×40 μm^2 was directed at the surface under an incident angle of 0.04° , which is close to the angle
75 of the total external reflection for Pd at this energy. A small penetration depth under grazing incidence allowed us to distinguish the diffraction signal from outermost atomic layers and study the atomic structure of the Pd(100) surface. The delivered flux was estimated to be on the order of 5×10^{10} photons/s. A large two-dimensional 410×410 mm² Perkin-Elmer detector with 200×200 μm^2
80 pixel size and adapted for X-rays with the energy higher than 20 keV was available for recording of diffraction patterns. The recorded data analysis procedure was described in detail in [11, 16]. A special UHV chamber allowing for surface cleaning *in vacuo* combined with a gas flow reactor for controlled gas exposure at pressure up to 1 bar was used [20].

Figure 1: (Color online) (a) LEED image (60 eV beam energy) of a clean metallic Pd(100) single crystal surface, (b) LEED image (43 eV beam energy) and (c) a schematic representation of the reciprocal in-plane structure of Pd(100)- $(\sqrt{5} \times \sqrt{5})\text{R}27^\circ\text{-O}$ surface oxide. Yellow arrows represent the reciprocal Pd(100) surface unit cell, light blue and red arrows represent two rotational domains of the surface oxide structure. (d) A schematic representation of the structure of PdO(101) unit cell in bulk PdO, (e) a schematic representation of a Pd(100)- $(\sqrt{5} \times \sqrt{5})\text{R}27^\circ\text{-PdO}(101)$ surface oxide structure. The $(\sqrt{5} \times \sqrt{5})\text{R}27^\circ$ unit cell is shown with a dashed rectangle. The atoms included in the cell are marked with plain color. The substrate unit cell is shown with a solid yellow rectangle.

85 The surface oxide structure in the LEED and STM experiments was formed
 by 10 min exposure of a Pd(100) to 5×10^{-5} mbar of O₂ at 573 K temperature
 and subsequently studied in UHV after cooling down to the room temperature.
 The SXRD experiments were performed for the structure produced in the same
 way but without cooling the sample down for the measurements and pumping
 90 the gas out of the chamber. In the case of HESXRD measurements a surface
 oxide was formed and investigated in a flow of 2 ml_n/min O₂ (1 ml_n is the
 amount of gas corresponding to 1 ml at standard pressure and temperature), 4
 ml_n/min CO and 25 ml_n/min Ar i.e. close to the stoichiometric ratio between
 CO and O₂ for complete oxidation to CO₂, at a sample temperature of 600 K.
 95 The total pressure in the reactor was 100 mbar.

To describe the crystal structure, a tetragonal set of basis vectors $\mathbf{a}_1, \mathbf{a}_2$
 lying in the surface plane and $\mathbf{a}_3$ perpendicular to them was used. In terms
 of the bulk lattice constant a_0 ($a_0(\text{Pd}) = 3.89 \text{ \AA}$) the lengths of these vectors
 can be expressed as $|\mathbf{a}_1| = |\mathbf{a}_2| = \frac{a_0}{\sqrt{2}} = 2.75 \text{ \AA}$ and $|\mathbf{a}_3| = a_0 = 3.89 \text{ \AA}$. The
 100 corresponding reciprocal lattice vectors are, thus, also mutually perpendicular
 and have the length of $|\mathbf{b}_1| = |\mathbf{b}_2| = 2.29 \text{ \AA}^{-1}$ and $|\mathbf{b}_3| = 1.62 \text{ \AA}^{-1}$.

The diffraction patterns calculated for the structural models evaluated in the
 work were produced using the software ROD by Elias Vlieg [21] and WINROD
 by Daniel Kaminski [22].

105 3. Results

3.1. Diffraction results

In Figure 1b, c, the observed LEED pattern and the corresponding schematic
 in-plane representation of the reciprocal lattice of a Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-
 PdO(101) structure grown in pure oxygen are shown. As was previously dis-
 110 cussed in [11, 14, 15, 16] a (1×2) unit cell of the PdO(101) mesh forms a super-
 structure on a Pd(100) surface with four 90° rotational and four mirror domains
 (making eight domains in total). In the side view of the PdO(101) structure
 (see Figure 1d) it can be recognized that oxygen atoms occupy sites above and

below the nearly planar Pd layer. According to our LEED measurements the superstructure seems uniform and regular, and no features deviating from perfect
115 $(\sqrt{5} \times \sqrt{5})R27^\circ$ pattern can be observed.

In Figure 2, a high-resolution in-plane scan of the reciprocal space around $H = 0.4$, $K = -0.8$, at $L = 0.1$ obtained by SXRD measurements of the same surface structure is shown. For the future comparison with HESXRD
120 experiments, it should be mentioned here that this scan was recorded in about 80 minutes. The regions of enhanced intensity in the figure represent the cross-sections of diffraction rods produced by the surface oxide. From a perfectly regular $(\sqrt{5} \times \sqrt{5})R27^\circ$ surface structure we expect to see one rod located exactly at $H = 0.4$, $K = -0.8$ position. Here, it is clearly visible, however, that an in-
125 plane splitting and a small shifting of the diffraction rod take place. It results in the appearance of two separate diffraction features with the in-plane positions of $H = 0.376$, $K = -0.811$ and $H = 0.404$, $K = -0.816$. Clearly, the resolution of our LEED instrument can not resolve the split peaks.

In the HESXRD experiments, the $(\sqrt{5} \times \sqrt{5})R27^\circ$ -PdO(101) structure on
130 the surface of a Pd(100) single crystal was studied *in situ* during CO oxidation at semirealistic conditions [16]. The expected positions of 43 superstructure diffraction rods were examined resulting in the detection of their splitting and shifting in a similar manner as in SXRD giving rise to 84 actual diffraction features. Half of the recorded data set is discussed in the current contribution
135 while the second half is omitted due to the four-fold symmetry of the system. To compare the time scale of these measurements with conventional SXRD, it should be mentioned that the whole data set can be recorded within 5–15 minutes making HESXRD a suitable technique for fast structure determination.

In Figures 3b and 3c, an integrated HESXRD image presenting the most
140 intense diffraction features collected during a 90° rotation of the sample under the X-ray beam (see [11, 16] for the details of the data treatment) and the corresponding in-plane cut through the reciprocal space integrated for L -values between 0 and 3 are shown correspondingly for the Pd(100)- $(\sqrt{5} \times \sqrt{5})R27^\circ$ -PdO(101) structure. Double and triple split features can be observed indicating

Figure 2: (Color online) A SXR in-plane scan around $H = 0.4$, $K = -0.8$, at $L = 0.1$ recorded with 10 keV photon energy at the Max Planck beamline (ANKA). The asymmetry of the spots is related to the strong beam divergence.

145 a more complex than $(\sqrt{5} \times \sqrt{5})\text{R}27^\circ$ structure of the surface oxide.

Two examples of split and shifted diffraction features are shown in two and three dimensions in Figure 4. The double feature around $H = 0.4$, $K = -0.8$ has the exact in-plane coordinates of $H = 0.371$, $K = -0.813$ and $H = 0.401$, $K = -0.819$, which perfectly matches the SXRD results obtained in pure oxygen. The region around $H = 0.8$, $K = -1.6$ shows a triplet diffraction feature with the exact positions of the peaks at $H = 0.739$, $K = -1.619$, $H = 0.800$, $K = -1.636$ and $H = 0.806$, $K = -1.605$.

3.2. STM results

Figure 5 shows a representative STM image recorded for a $\text{Pd}(100)-(\sqrt{5} \times \sqrt{5})\text{R}27^\circ\text{-PdO}(101)$ structure grown in pure oxygen. An overall well ordered surface oxide layer is perturbed by regions of distorted periodicity similar in shape, apparent structure and orientation. Three stripes of distorted periodicity aligned approximately along the $[011]$ crystallographic direction of the substrate with a width of about 10–15 Å in $[01\bar{1}]$ direction are indicated by white arrows in the image. Such stripes were observed in all STM images recorded for this system. In larger scale STM images (not shown here) one can see that these regions of structural distortion are embedded in the oxide layer over the whole surface, and exhibit a fairly regular arrangement and the same orientation within a domain. The distance between the stripes varies within about 15 Å and is around 50 Å on the average. The appearance of the stripes has previously been discussed in ref [15], and provides a direct view of the mismatch between the $(\sqrt{5} \times \sqrt{5})\text{R}27^\circ\text{-PdO}(101)$ and $\text{Pd}(100)$, and an important clue to the origin of the observed split peaks in the diffraction data.

3.3. Discussion

170 It is clear that the observed diffraction patterns obtained from both SXRD and HESXRD experiments deviate from the perfect $\text{Pd}(100)-(\sqrt{5} \times \sqrt{5})\text{R}27^\circ\text{-PdO}(101)$ positions in reciprocal space. Based on our analysis of the in-plane diffraction patterns, we find that they could be produced by a superstructure

Figure 3: (Color online) The part of the integrated HESXRD scan of (a) a clean metallic Pd(100) single crystal surface, (b) a Pd(100)- $(\sqrt{5} \times \sqrt{5})R27^\circ$ -PdO(101) structure. (c) An in-plane cut through the HESXRD data set integrated for L -values between 0 and 3 collected for a Pd(100)- $(\sqrt{5} \times \sqrt{5})R27^\circ$ -PdO(101) structure (the background has been removed and black rings mark the positions of the diffraction maxima to facilitate the visibility of the pattern). Yellow rectangles 1 and 2 in panels *b* and *c* indicate the positions of two diffraction rods arising from the surface oxide (presented separately in Figure 4). Black hexagons in panel *c* indicate the Pd(100) crystal truncation rods positions.

Figure 4: (Color online) 2D and 3D representations of the diffraction rods produced by Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-PdO(101) structure and located at around (a) (0.4; -0.8; L) and (b) (0.8; -1.6; L). The images enlarge the areas marked with rectangles 1 and 2 in Figure 3b, c.

Figure 5: (Color online) An atomically resolved STM image (0.6 V and 0.85 nA) of the Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27 $^\circ$ -PdO(101) structure. White bold arrows indicate the stripes of distorted periodicity. Solid black line indicate a row of Pd atoms, which preserve their two-oxygen-coordination on both sides of the region of distorted periodicity (note a slight downward shift of the row on the right side). Solid blue line shows an atomic row, where the coordination is switched from two to four oxygen from left to right side of the distortion region. The inset shows the relation between the image and the atoms of the surface oxide [15].

with a slightly distorted surface unit cell and four domains (see Figure 6a).

175 The other four domains can be omitted since their contribution to the in-plane periodicity is redundant due to the symmetry.

Based on the positions of the diffraction features, the real space lattice parameters of the surface oxide for this monoclinic structure can be calculated as $|\mathbf{a}_1^*| = 6.20\text{\AA}$ and $|\mathbf{a}_2^*| = 6.02\text{\AA}$. The angle between $\mathbf{a}_1^*$ and $\mathbf{a}_2^*$ can also be
 180 calculated to be 88 $^\circ$ in real space (see Figure 6d). These values, therefore, deviate from a non-distorted orthogonal Pd(100)-($\sqrt{5} \times \sqrt{5}$) superstructure unit cell with the lattice constant $a_S = 6.151\text{\AA}$.

The comparison of the experimental data and results calculated using the distorted unit cell model was done for more than one hundred diffraction features
 185 obtained by SXRD and HESXRD (not shown here). This model explains well the in-plane splitting and shifting of the diffraction rods at almost all reciprocal positions. One example is shown in Figure 6b. The model, therefore, can

Figure 6: (Color online) (a) A schematic representation of reciprocal in-plane lattice of the superstructure with a slightly distorted $(\sqrt{5} \times \sqrt{5})R27^\circ$ unit cell (demonstrated in panel d) and four domains (red = $(1, 0, 0, 1)$, blue = $(0, -1, 1, 0)$, purple = $(-1, 0, 0, 1)$, green = $(0, 1, 1, 0)$). (b-c) Close-ups of the HESXRD features around $H = 0.4$, $K = -0.8$ and $H = 0.8$, $K = -1.6$ together with the positions of the corresponding diffraction features (marked with crosses) calculated for the distorted unit cell. Black arrow in panel c indicates the reflection that is not explained by the model. (d) A schematic representation of both the $(\sqrt{5} \times \sqrt{5})R27^\circ$ and the distorted unit cells in real space with underlying Pd(100) substrate.

be accepted as a better explanation of the Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-PdO(101) structure in comparison with the simple ($\sqrt{5} \times \sqrt{5}$)R27° periodicity reported previously.

There is more to discuss, however, regarding the long-range periodicity of the PdO(101) surface oxide on Pd(100). Firstly, although the majority of the diffraction features are adequately predicted by the calculations based on the distorted unit cell, there is an exception. Namely, the triplet diffraction features observed at several positions include two split rods explained by the model and one weak spot each that does not have a calculated analog. In Figure 6c the black arrow indicates a weak reflection, which is not predicted by the proposed model, in the area located around $H = 0.8$, $K = -1.6$.

Secondly, the regular regions of distorted periodicity observed in STM are not accounted by the proposed model in any way. These stripes appear to be similar to structural distortions observed for numerous incommensurate surface structures [23, 24, 25, 26] and can be attributed to the lateral stress accumulating due to a non-perfect match between the surface structure and the substrate. This tension needs to be released regularly in order to preserve the superstructure periodicity. The Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-PdO(101) structure was indeed shown to be incommensurate with the substrate along the $[01\bar{1}]$ direction [15]. In order to correct for the accumulating stress, the superstructure lattice should shift laterally restoring the relative positions of the Pd atoms of the oxide and the substrate.

Looking at the black line drawn in Figure 5, one can notice that, upon crossing the distortion region, the bright row constituted of the Pd atoms of the PdO coordinated to two oxygen atoms continues as the same bright row, pointing at the same coordination of the Pd atoms on both sides of the stripe with a small shift downwards on the right side. At the same time, following the blue line in the same image, one can notice the alternation of the rows of Pd atoms, which are coordinated to two oxygen atoms on the one side and to four oxygen atoms on the other side of the region of the distortion, clearly indicating the vertical shift of the structure. Relying on the STM images, one can suggest

that the shift occurs approximately along the $[011]$ substrate direction.

220 Further we propose a qualitative model that could explain both the regular distorted regions in STM images and additional reflections in the diffraction patterns. The model is based on a larger superstructure unit cell comprising the long-range periodicity of the PdO(101) surface oxide on Pd(100). The size of the unit cell is optimized to fit the diffraction data, which averages the periodicity
225 of the stripes over the whole surface exposed to the incoming beam. In the STM images this periodicity varies within about 15 Å, which means that the size of the superstructure unit cell can also vary. Thus, the proposed model qualitatively illustrates the principle of the $(\sqrt{5} \times \sqrt{5})R27^\circ$ -PdO(101) surface oxide periodic distortion due to the long-range incommensurability with the
230 Pd(100) substrate.

Figure 6d schematically shows the comparison of the distorted and the perfect $(\sqrt{5} \times \sqrt{5})R27^\circ$ unit cells on a larger scale. It can be seen that the further along the $[01\bar{1}]$ direction of the substrate the distorted structure expands the more downwards along the $[011]$ direction the atoms shift. Every fourteen substrate unit cells the structure shifts by about a half of the substrate in-plane
235 Pd-Pd distance (full distance is 2.75 Å). It can be noticed that in the right close-up of the Figure 6d the blue line ends at a bridge site while the red line ends between a four-fold hollow and a bridge site closer to the latter. Considering the fact that the structure is incommensurate only along one direction, however, it is
240 possible to assume that the lateral shift of the atoms occurs precisely along the $[011]$ substrate direction, meaning from a bridge to a four-fold hollow site. This assumption is supported by the appearance of STM images, where the stripes of distorted intensity are aligned with the $[011]$ substrate direction. It is also logical to assume that together with this lateral shift the height of the surface
245 oxide atoms along the surface normal will also change since the corresponding local arrangement of the substrate atoms changes.

The (5×5) coincidence unit cell was considered lately for the structural investigation of the Pd(100)- $(\sqrt{5} \times \sqrt{5})R27^\circ$ -PdO(101) [16]. Since the surface oxide lattice is incommensurate only in one direction it is reasonable to leave

250 one of the dimensions of the larger unit cell to be equal to the previously found value. Assuming further that every fourteen substrate unit cells the surface oxide atoms shift laterally by $1.375\text{\AA}$ (from a bridge to a four-fold hollow site), one can suggest this to be the second dimension of a larger unit cell. Therefore, models based on a larger unit cell with the width of fourteen and the height of
 255 five substrate unit cells were considered for the examination.

Out of several candidates that were examined, the best fit to the experimental data was achieved for a non-orthogonal unit cell described by the matrix $\begin{pmatrix} 14 & -1 \\ 0 & 5 \end{pmatrix}$ with respect to the substrate unit cell. Several variants of the internal unit cell structure comprising the lateral shift of the surface oxide atoms
 260 were compared. It should be mentioned that, although we consider a larger superstructure unit cell, on the average it is equivalent to the previously discussed small distorted unit cell and therefore is not supposed to produce significantly different diffraction pattern. However, the fine details will be different due to a more complex internal structure of the larger cell.

265 In Figure 7 three structural models finally considered in the current contribution are shown. They are referred to as *s0*, *s5* and *s15* depending on the sharpness of the lateral shift of the surface oxide lattice. The Pd atoms in PdO shift downwards along the $[011]$ direction every fourteen substrate unit cells by half of the substrate Pd–Pd distance ($1.375\text{ \AA}$). The out-of-plane positions of
 270 Pd atoms are varied within $0.2\text{ \AA}$ as it was previously found for the perfect $(\sqrt{5} \times \sqrt{5})R27^\circ$ model [15, 16]. However, since the local atomic arrangement of the substrate varies with the lateral shift of the surface oxide atoms, the out-of-plane displacement is distributed over the larger unit cell correspondingly to the underlying substrate to emulate the long-range film undulation. For every
 275 model from left to right side, the sequence of two-oxygen-coordinated Pd atoms is preserved in the row along black lines and the switch between two- and four-oxygen-coordinated Pd atoms can be seen along blue lines. This matches the STM image in Figure 5 and supports the assumption that the atoms shift precisely along the $[011]$ substrate direction switching between bridge and four-

280 hollow sites.

In the *s0* model, only the first and the last atom of the color coded Pd row are in the ideal bridge and four-fold hollow positions and a gradual transition occurs along the row. This model most closely matches the model with the small distorted unit cell. In the *s5* and *s15* models more atoms are left in the ideal
285 $(\sqrt{5} \times \sqrt{5})R27^\circ$ positions and the transition becomes sharper and sharper. The atomic displacements in all models are calculated by application of the Gauss error function with different level of sharpness to the atoms between the first and the last positions in a row.

All three models were examined and used to calculate their corresponding
290 in-plane diffraction patterns, which were then compared with the experimental data. Since the out-of-plane variation of the diffracted intensity along the rods depends on the vertical displacements of the surface oxide atoms, which are not known, we have integrated the in-plane patterns calculated for the models for *L* values between 0 and 3 as it was done with the experimental data to
295 obtain the HESXRD in-plane pattern in Figure 3c. In this way, regardless of the out-of-plane shape of the rods, their in-plane positions are observable.

The examples of two split rods and the corresponding diffraction features obtained from the models are shown in Figure 8. To produce the patterns, the same four domains as was previously discussed were considered. It can be seen
300 from the figure, that different rotational orientation of the structural domains can actually explain all split diffraction features. It is also clear that the *S0* model fails to reproduce all the experimental diffraction peaks in the same way as was concluded before for the small distorted unit cell, leading us to abandon this structural model to explain the observed diffraction. For the *s5* and the *s15*
305 models, all diffraction peaks can be reproduced. It can be seen, however, that the intensity ratio between the split diffraction features is best explained by the *s5* model, which also better represents the appearance of the STM images. Therefore, we conclude that this model qualitatively explain the fine details of the experimentally measured diffraction features and does not contradict with
310 the average distance between surface oxide distortions found in STM studies.

Figure 7: (Color online) s0, s5 and s15 structural models.

Figure 8: (Color online) Enlarged areas of Figure 3c in the vicinity of $H = 0.4$, $K = -0.8$ and $H = 0.8$, $K = -1.6$. The crosses represent the positions of diffraction rods calculated for the s0, s5 and s15 models, the size of the crosses is proportional to the calculated intensity of the respective diffraction features. Different color of the crosses indicate the contribution from different domains of the surface structure.

The width of fourteen substrate unit cells is equal to 38.5 Å, which is less than the average distance between the stripes of distorted periodicity observed in the STM studies by 23%. One possible argument that can be used to explain this discrepancy, is that STM probes the surface locally while diffraction techniques average the structural information over the whole surface. In the case if the periodicity of the distortion regions is not so strict, the average distance may deviate from that locally observed by STM. Additionally, the diffraction and STM studies were performed under different conditions, in particular temperature, which might cause fine deviations between the structures observed in these experiments. Significant structural difference is, however, excluded by previous studies [15, 16].

There are several important conclusions that can be drawn from this study. The first is that, without access to Spot Profile Analysis (SPA) LEED instrumentation, the high resolution from SXRD is absolutely necessary to detect the deviations from the perfect Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-PdO(101) structure. A second conclusion is that the use of high energies in SXRD combined with a large area detector greatly facilitates the task to measure these subtle deviations, without a significant loss in resolution. In this way, the data collection rate increases enormously when mapping reciprocal space compared to traditional SXRD methods. In fact, without the use of HESXRD in the present study, and the facile data collection, such subtle structural differences would have been overlooked.

Finally, it is interesting to observe that only the correct internal structure of the unit cell allowed us to reproduce all the experimental observed diffraction peaks. Obviously, this is not surprising, and has been used for structure determinations for many years, however, it is satisfying to observe these effects on a extremely subtle case as reported in the present work.

4. Summary

To conclude, we have quantitatively and qualitatively refined the structure of the Pd(100)-($\sqrt{5} \times \sqrt{5}$)R27°-PdO(101) and have found a qualitative structural model explaining the fine details of the diffraction data and long-range order periodic features observed in STM images simultaneously. Using a large non-orthogonal unit cell described by the matrix $\begin{pmatrix} 14 & -1 \\ 0 & 5 \end{pmatrix}$ with respect to the substrate unit cell, we have shown that the one-direction incommensurability of the surface oxide can be released in the long range by shifting of the superstructure lattice along the [011] or the [01 $\bar{1}$] (depending on the domain orientation) substrate direction by the half of the substrate unit cell. The transition region can be well described by the shape of the Gauss error function with a medium sharpness involving about seven Pd atoms. On the average this model is equivalent to a simpler model based on a distorted ($\sqrt{5} \times \sqrt{5}$)R27° unit cell with the $|\mathbf{a}_1^*| = 6.20\text{\AA}$ and $|\mathbf{a}_2^*| = 6.02\text{\AA}$ basis vectors with the angle 88° between them. This simplified model does not, however, explain the triple features of the high-resolution diffraction in-plane patterns and regions of distorted periodicity embedded in the oxide layer over the whole surface area observed in STM.

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