The two-dimensional cobalt oxide (9 × 2) phase on Pd(100)

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The two-dimensional (2D) Co oxide monolayer phase with (9 × 2) structure on Pd(100) has been investigated experimentally by scanning tunneling microscopy (STM) and theoretically by density functional theory (DFT). The high-resolution STM images reveal a complex pattern which on the basis of DFT calculations is interpreted in terms of a coincidence lattice, consisting of a CoO(111)-type bilayer with significant symmetry relaxation and height modulations to reduce the polarity in the overlayer. The most stable structure displays an unusual zig-zag type of antiferromagnetic ordering. The (9 × 2) Co oxide monolayer is energetically almost degenerate with the c(4 × 2) monolayer phase, which is derived from a single CoO(100)-type layer with a Co3O4 vacancy structure. Under specific preparation conditions, the (9 × 2) and c(4 × 2) structures can be observed in coexistence on the Pd(100) surface and the two phases are separated by a smooth interfacial boundary line, which has been analyzed at the atomic level by STM and DFT. The here described 2D Co oxide nanolayer systems are characterized by a delicate interplay of chemical, electronic, and interfacial strain interactions and the associated complexities in the theoretical description are emphasized and discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3578187]

I. INTRODUCTION

Two-dimensional (2D) layers derived from transition metal oxides are interesting systems of study, since fundamentally new concepts of structure, bonding, and elastic behavior can be supported. 2D layers typically require a substrate for stabilization and accordingly they may be regarded as hybrid systems, such as metal-oxide hybrid systems, if the oxide layer is supported on a metal surface.1–4 One such system formed by the deposition of an oxide monolayer (ML) onto a metal single crystal surface is essentially the realization of an isolated 2D metal-oxide interface, which however is not coupled to an oxide bulk phase. The absence of the latter is decisive, since interfacial chemical bonding to the substrate, charge transfer, metal screening, and low dimensionality effects in general may become dominant, thus creating novel systems of materials with often unprecedented and peculiar properties.1–7 For example, the structure and stoichiometry of 2D oxide overlayers may be significantly different from known bulk oxide phases, and the structure–property relation of physical response may give rise to unexpected electronic, magnetic, and chemical behavior. This is illustrated here with the 2D Co oxide layers that grow on a Pd(100) surface.

Cobalt oxides have found interesting applications in many diverse fields of the advanced technologies,8 and the epitaxial growth of Co oxide thin films has been reported on various metal substrates, such as Ag(100),9–13 Ir(100),14–18 and Pd(100).8 A variety of different structures and phases have been described as a function of film thickness: while for thicker films (>10 ML) the oxide overlayers converge to the known bulk phases of CoO and/or Co3O4, the films in the ultrathin limit of 2D structures depend on the particular metal substrate and the thermodynamic and kinetic parameters of the deposition. On Ag(100) the first monolayer appears to grow pseudomorphically in CoO(100) form9,12 since the lattice mismatch to the bulk-type CoO(100) surface is moderate (~4%), but the wetting properties of this first layer are poor. Conversely, on the nonreconstructed Ir(100)14 × 1 substrate, which has a ~11% lattice mismatch to the bulk-type CoO(100) surface, growth of CoO(100) has not been observed but a complex c(10 × 2) CoO coincidence structure has been reported for the first wetting layer, which has been interpreted in terms of a structure related to a CoO(111) phase.14,18 On Pd(100), two well-defined wetting layer phases have been detected around one monolayer coverage with c(4 × 2) and (9 × 2) surface structures.8 The thickness-dependent structural evolution of Co oxide nanolayers on Pd(100) from low coverages up to 20 ML thick films has been reported in a recent publication, where the growth parameters of various phases have been established.8

Here we concentrate on the 2D monolayer regime and, in particular, investigate the structure and the physical properties of the (9 × 2) cobalt oxide phase by experimental and theoretical means; moreover, its relation to the 2D c(4 × 2) Co oxide phase will be addressed. Of special interest in this context is the one-dimensional (1D) interface which is formed between the (9 × 2) and the c(4 × 2) monolayer phase: the latter can be prepared on the Pd(100) surface in coexistence with the (9 × 2) structure under appropriate kinetic conditions. The c(4 × 2) periodicity with a formal Co3O4 stoichiometry...
has been shown recently to arise from a periodic array of Co vacancies, which are created in a pseudomorphic CoO(100) monolayer to partially compensate for the strain associated with the lattice mismatch between cobalt monoxide and the Pd substrate, which is ∼9% for bulk CoO but is expected to be reduced at the ML level. The c(4 × 2) oxide structure appears to be a prototypical phenomenon of the 2D phases of rock-salt structure monoxides supported on transition metal surfaces, since analogous Ni₃O₂ and Mn₃O₄ phases have also been observed on the Pd substrate.

In this work, we use high-resolution scanning tunneling microscopy imaging to characterize the structural aspects of the (9 × 2) monolayer phase and of the 1D interface between the (9 × 2) and c(4 × 2) phases. For completeness, we also briefly recall the essential elements of the c(4 × 2) structure. Density functional theory (DFT) is used to derive the ground state structure, the energetics, and the electronic and magnetic properties of the (9 × 2) phase. We find that its structure has a peculiar hybrid polar/nonpolar character in which the heights of Co and O atoms with respect to the metal support present a wavy modulation as a way to achieve strain release. We report an unusual antiferromagnetically ordered ground state for the (9 × 2) phase and emphasize the theoretical challenges in modeling a large unit cell coincidence structure of a highly correlated material. Our methodology is detailed in Sec. II, results are presented and discussed in Sec. III, and conclusions summarized in Sec. IV.

II. EXPERIMENTAL AND THEORETICAL METHODS

The STM measurements have been carried out in a custom-designed variable-temperature STM system (Oxford Instruments), equipped with the typical facilities for sample manipulation and cleaning and for physical vapor deposition. Apart from the STM stage the system comprises a CMA for Auger electron spectroscopy, a low-energy electron diffraction (LEED) optics, electron beam evaporators, and a quartz microbalance. For the present measurements, the STM was operated at room temperature in constant current mode using electrochemically prepared W tips, which have been cleaned in situ by electron bombardment. Detailed tunneling conditions are given at the respective images, with positive sample bias leading to empty electron state imaging of the sample. The sample work function has been measured by the low-energy secondary electron cut-off in UV photoelectron spectra, which have been recorded in a dedicated photoelectron spectrometer system.

Clean Pd(100) substrate surfaces have been prepared by cycles of Ar ion sputtering (1 keV) and annealing at 1000 K. Periodically, the crystal was exposed to oxygen at 570 K followed by a brief flash to 950 K in vacuum to remove residual carbon contamination. The Co oxide phases have been created by reactive evaporation of Co, 0.75–1 ML (1 ML is defined by the density of surface atoms of Pd(100), i.e., 1.32 × 10¹⁵ Co atoms/cm²), from an electron beam evaporator in 1 × 10⁻⁶ mbar O₂ with the substrate kept at room temperature. The surface temperature deposition was followed by 5–10 min annealing at 570 K or at 670 K in 1 × 10⁻⁶ mbar O₂, in order to create the c(4 × 2) and (9 × 2) structures, respectively. By careful tuning of the oxidation conditions in between these limiting values the c(4 × 2) and (9 × 2) structures could be attained in coexistence at the Pd(100) surface.

DFT calculations were performed using the QuantumEspresso package, employing a basis set of plane waves, ultra-soft pseudopotentials, and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation (xc-) functional. A DFT + U approach was also employed in selected calculations. The unit cell was modeled by taking a (9 × 2) portion of the Pd(100) surface extending 5.6 Å along the x axis and 25.2 Å along the y axis. The first-neighbor distance in the metal support was set to 2.80 Å, corresponding to the equilibrium lattice parameter of bulk Pd according to our DFT approach, to be compared with an experimental value of 2.75 Å. The metal support was modeled by four Pd slabs in (100) stacking, where the bottom two layers were kept frozen in their bulk lattice positions. The oxide monolayer was described by organizing 16 Co and 16 O atoms in four alternating rows running along the longer axis of the unit cell (see Fig. 4) and relaxing the structure until the forces on the oxide atoms resulted smaller than 0.01 eV Å⁻¹. Along the z axis, a minimum empty space of 15 Å was chosen to avoid interactions between replicated cells. A dipole correction was applied to cancel spurious coulombic interactions among replicated images. Values of 40 and 400 Ry were chosen as the energy cutoff for the selection of the plane waves for the description of the wave function and the electronic density, respectively. The first Brillouin zone was k-sampled by employing a (4, 1, 1) grid and the electronic levels were broadened with a Gaussian smearing of about 0.03 eV. All the calculations were performed spin-polarized. STM images were simulated applying the Tersoff–Hamann approach at a constant height of about 2 Å above the oxide surface (this small height value is justified by the very low bias at which the STM images were simulated).

Selected calculations on the (9 × 2) phase were also performed using a hybrid B3PW91 xc-functional and an approach adopting a basis set of Gaussian-type orbitals (GTO). By using the geometry optimized at the DFT/PBE level, self-consistent energy calculations were performed and STM images were simulated using the CRYSTAL06 package. In addition to the calculation of the Hartree–Fock component, the GTO procedure entails a truly 2D approach to the electronic problem avoiding the definition of a vacuum layer and the interaction of the system with its periodic images. The basis sets here employed consisted of an all-electron 8–411G* basis set for oxygen and s/4sp/2d basis set for cobalt. For Pd, only the 18 outermost electrons were explicitly described via a basis set consisting of 4sp/2d GTO, while a small-core pseudopotential was chosen to replace the frozen innermost electrons. Values of (7, 7, 7, 15) for the tolerances defining the reciprocal space integration was performed by sampling the Brillouin zone at a mesh of points defined by shrinking factors set equal to 4 and 1. As the aim of the hybrid-DFT calculations was to investigate the effect of a different xc-functional on the simulated STM images, the basis sets used in the energy evaluation was enriched by...
s-type ghost-functions with exponents of 0.08 a.u located 2.0 Å above all the surface oxide atoms in order to correctly describe the tails of the local DOS outside the surface.

III. RESULTS AND DISCUSSION

A. Experimental results

Figure 1(a) shows a large-scale topographic STM image of the \((9 \times 2)\) structure, while Fig. 1(b) displays a selected area at higher magnification. In the upper right-hand-side corner of image (a) a boundary to a small area of \(c(4 \times 2)\) structure is visible, and two anti-phase domain boundaries within the \((9 \times 2)\) area (marked by arrows) are also recognized. The \((9 \times 2)\) structure forms a well-ordered flat wetting layer with rodlike maxima in STM that are arranged in rows along the [011] direction of the Pd substrate. At higher magnification (achievable only at very low sample bias, image b) the rodlike maxima are resolvable into four bright atomic-size spots separated by four darker protrusions, thus forming rows of maxima running along the [011] azimuth of the Pd(100) surface. The STM maxima are equidistantly spaced by \(a = 3.1 \pm 0.1\) Å, and the rows along [011] are separated on average by \(2.75 \pm 0.1\) Å; the latter is equal to the lattice constant of Pd(100) \(a_{\text{Pd}}\). The intensity modulations along the rows define a unit cell B, see Fig. 1(b), with a periodicity \(m = 24.8 \pm 0.2\) Å along [011]; since each row is shifted by \(a_{\text{Pd}}/2\) along [011] with respect to the adjacent row, unit cell B has a periodicity of \(5.5 \pm 0.1\) Å along [011]. An alternative primitive unit cell C, joining nearest-neighbor protrusions irrespective of their intensity, defines a quasihexagonal overlayer lattice with average lattice parameters \(c = 3.2 \pm 0.1\) Å and \(a = 3.1 \pm 0.1\) Å. Close inspection of STM images such as in Fig. 1(b) reveals that the chains of maxima along [011] display a slight periodic modulation in their lateral position (i.e., in [011] direction), creating a wavy line of protrusions along [011]. Unit cell B with average dimensions \(24.75 \times 5.5\) Å describes the superperiodicity of the brightest maxima and may be related to the underlying Pd(100) lattice in terms of a \((9 \times 2)\) cell, with additional bright maxima close to the center but shifted by \(\pm a_{\text{Pd}}/2\) from the true centered position. Since eight atom-like STM protrusions match \(9 \times a_{\text{Pd}}\) in unit cell B \((8.3 \times 3.1\) Å \(\approx 9 \times 2.75\) Å), the \((9 \times 2)\) structure is most naturally associated with an \((8 \times 9)\) coincidence lattice.

Figure 2 shows an STM image and a corresponding DFT derived model of the \((4 \times 2)\) structure, which has been associated with a pseudomorphic CoO(100)-type monolayer.\(^{19}\) The \((4 \times 2)\) unit cell is formed by a rhombic array of \(1/4\) of a ML of Co vacancies, which are created to partially compensate for the compressive interfacial strain; this results in a formal stoichiometry of CoO\(_2\). The details of the \((4 \times 2)\) model have been discussed in a previous publication.\(^{10}\) We recall here that the bright protrusions are associated with the Co atoms, whereas the dark holes represent Co vacancies; according to DFT, the oxygen atoms are not imaged in the STM under the tunneling conditions of Fig. 2(a).

The \((9 \times 2)\) structure can be prepared in coexistence with the \((4 \times 2)\) structure at the same surface under appropriate kinetic conditions (see Sec. II), forming a well-defined 1D interface boundary (see Fig. 3). This 1D interface bears two interesting aspects, concerning: (i) the smooth transition from one structure into the other and (ii) the nature of species being imaged in the STM. In Fig. 3, STM images of the \((9 \times 2)\)/\((4 \times 2)\) boundary region are shown, recorded under different tunneling conditions. To address the first aspect, consider Fig. 3(a) which displays the \((4 \times 2)\) region on the right hand side. As mentioned above, the dark depressions in the STM image form the primitive rhombic unit cell of the \((4 \times 2)\) structure, which has been associated with a pseudomorphic CoO(100)-type monolayer.\(^{19}\) The \((4 \times 2)\) unit cell is formed by a rhombic array of \(1/4\) of a ML of Co vacancies, which are created to partially compensate for the compressive interfacial strain; this results in a formal stoichiometry of CoO\(_2\). The details of the \((4 \times 2)\) model have been discussed in a previous publication.\(^{10}\) We recall here that the bright protrusions are associated with the Co atoms, whereas the dark holes represent Co vacancies; according to DFT, the oxygen atoms are not imaged in the STM under the tunneling conditions of Fig. 2(a).

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\[ \text{FIG. 4. (a) Side view of the (9 × 2) unit cell, showing a Pd–Co–O stacking; (b) top view of four unit cells of the (9 × 2) phase. Pd atoms are depicted in white; O atoms in light gray (yellow in color); Co atoms in dark gray with different shades (blue and red in color), reflecting the AFM_3 magnetic ordering of the CoO monolayer.} \]

The (9 × 2) structure as indicated in the figure. Close to the boundary to the (9 × 2) phase, the dark depressions associated with vacancies form a new square structural motif, as highlighted by dashed lines on the image. The formation of this square arrangement of vacancies is always associated with a defect in the vicinity of the square with a less dark contrast in the STM (see ellipses on the image), which provides the necessary shift of the vacancy position from rhombic to square. Although the nature of this defect cannot be derived from the STM images, it is speculated that it may contain an extra Co species, which leads to a local reduction of the CoO\(_2\) stoichiometry. This local reduction close to the interface may contribute to the formation of a very smooth boundary and suggests that the (9 × 2) phase is in a lower oxidation state than the c(4 × 2) phase. This is indeed confirmed by the DFT calculations (see below).

In the STM image of Fig. 3(b) we address the question of how the bright lines of protrusions without vacancies (see arrows), suggested to represent the Co atoms of the CoO\(_2\) phase, transform from the c(4 × 2) into the (9 × 2) structure. At the interface, e.g., in the encircled regions, the bright maxima appear to belong to both structures. For example, the spots marked with a cross seem to terminate the close-packed Co rows of the c(4 × 2) structure in the [011] direction, but appear to belong also to the rows of bright protrusions along the [011] direction of the (9 × 2) structure. Prima facie, this would suggest, assuming that the Co atoms are imaged bright in the c(4 × 2), that they are also imaged with bright contrast in the (9 × 2) structure. However, as discussed below, the situation is subtle and the analysis requires a more refined theoretical treatment.

**B. Theoretical analysis**

Based on the suggestions from the experimental STM images, a (9 × 2) oxide monolayer was built by organizing 16 Co and 16 O atoms in four alternating rows running along the longer axis of the unit cell described in Sec. II, see Fig. 4. The Co atoms are in contact with the metal surface and are arranged according to a close-packed pattern, while the O atoms occupy half of the hollow sites left by the Co lattice: in this way each ion has three counterions as first neighbors and six like ions as second neighbors. Due to the (8 × 9) coincidence lattice, the in-plane positions of the Co (O) atoms with respect to the position of the metallic Pd atoms underneath vary: the Co atoms at the boundary of the cell are in a bridge position between two Pd atoms, while the Co atoms in the middle of the cell occupy hollow sites on the (100) surface. This structure was locally relaxed and then subjected to a short run of Car–Parrinello dynamics, verifying that it represents a robust local minimum on the system potential energy surface.

Co being a magnetic atom, the magnetic state of the (9 × 2) phase was investigated by testing three different possible arrangements of the Co spins: (i) a ferromagnetic (FM) arrangement; (ii) an antiferromagnetic order (AFM_2) in which Co ions with parallel spin orientation are aligned along the long edge of the unit cell; (iii) an antiferromagnetic order (AFM_3) in which ions with parallel spin orientation are arranged in a zig-zag fashion running parallel to the short side of the unit cell—see Fig. 4(a), with Co ions depicted in different shades of darker gray (blue and red in color) according to the orientation of their spin. The AFM_3 arrangement, previously considered in a FeO ML grown on Pt(111), was found to be the ground state, with AFM_2 higher in energy by 0.11 eV per CoO unit and FM higher by 0.17 eV per CoO unit. The geometrical structure of the oxide phase is, however, only marginally affected by its magnetic order, as the three phases exhibit very similar equilibrium geometrical parameters. For all three phases, a Lowdin population analysis reveals that the charge state of the Co ions is about +0.95 ± 1.0 with a 3\(d^8\) electronic configuration implying the presence of two unpaired electrons (and thus two Bohr magnetons of magnetization) per Co center. This charge state is smaller than the formal one (+2). This—together with the minor charge transfer from the metal support (see below)—implies that the oxygens are not fully reduced. In contrast, it can be recalled that the c(4 × 2) phase has a ferromagnetic ground state. In the c(4 × 2) phase, the presence of lines running along (100) directions, in which half the Co ions are missing, reduces the magnetic coupling of the remaining ions and produces a stronger mixing with the electronic states of the support (metallization) than in the (9 × 2) phase, which is a bit more similar to bulk CoO.

It is interesting to estimate the relative stability of the (9 × 2) and the c(4 × 2) phases. We consider the following reaction:

\[
\frac{3}{8} \text{[CoO}(9 \times 2)/\text{Pd}(100)] + \frac{1}{2} \text{O}_2 + \frac{5}{8} \text{Pd}(100) \rightarrow \text{Co}_3\text{O}_4/\text{Pd}(100),
\]

\[
(9 \times 2) \text{AFM}_3 + c(4 \times 2) \text{FM},
\]
in which the formation of the c(4 × 2) phase is seen as an oxidation process of the CoO (9 × 2) phase (a proper amount of Pd surface is introduced to take into account the difference in density between the two phases). In the experimental annealing conditions (T = 600 K and p = 10^{-6} mbar) and estimating the Gibbs free energy of O2 by assuming an ideal gas behavior, the Gibbs free energy of the reaction amounts to +0.06 eV per Co atom. This small value indicates a slight thermodynamic preference for the CoO (9 × 2) phase but, at the same time, suggests a likely competition between the two phases, as experimentally confirmed by their coexistence. By decreasing the temperature, or increasing the O2 pressure, the sign of the Gibbs free energy of the reaction can be reversed in favor of the c(4 × 2) phase.

To understand the simulated STM images, it is important to observe that the Pd–Co–O stacking in the relaxed (9 × 2) structure is such that the Co atoms are positioned at about 2.13 Å above the Pd surface while the O atoms are about 0.5 Å above the Co atoms. The interplane Co–O distance and consequently the polar character of the film is thus appreciably reduced with respect to the (111) stacking in the bulk, about 1.2 Å. Moreover, both the Co and the O layers develop a wavy modulation of the height with an amplitude of 0.12 and 0.18 Å, respectively (the amplitude is calculated as the maximum difference in height between atoms of the same type).

This wavy modulation in height is at the basis of the brightness modulation in the simulated STM images, see Fig. 5, where the intensity of the bright spots correlates with the height of the O atoms in the cell. The experimental and simulated STM images shown in Fig. 1(b) and in Fig. 5(a) are in a fair agreement. However, at variance with the experimental suggestion the O atoms (and not the Co atoms) are mostly visible in the STM. To rationalize this result, we analyzed both the geometrical and the electronic structure of the oxide. In Fig. 5(a), the projected density-of-states (PDOS) is shown together with the STM image simulated at a bias of +80 meV; it can be observed that the major contribution at the Fermi level is given by the Co 3d minority states, whereas the O states (originating from the 2p band) are mainly located between −7.0 and −4.0 eV below the Fermi energy. Nevertheless, the Co atoms are visible in the simulated STM image only as faint spots, whereas the bright spots correspond to the O atoms. This is due to the difference in height between the two species and to the fact that the tunneling states on the O atoms are much more diffuse as these carry a negative charge. In contrast, in the c(4 × 2) phase Co and O ions lie at roughly the same height and Co is in a higher oxidation state so that Co is imaged as brighter in STM at the experimental bias.

In this connection, it can be noted that a related structure has been observed in the case of cobalt oxide grown on Ir(100), where the formation of a (10 × 2) ML phase has been shown and characterized via an analysis of the experimental low-energy electron diffraction (LEED) spectra. In the STM images of that phase a modulation with an alternation of four bright and five darker spots was found, in strong analogy with the brightness modulation found in the present (9 × 2) case. On the basis of LEED data, the authors suggested that the structure presents a smooth modulation of the height of the Co atoms within the cell and two distinct groups of O atoms characterized by quite different heights. They also proposed that the bright spots correspond to Co atoms and that the modulation of their height is the origin of the modulation in brightness in the STM images, although no theoretical analysis was presented.

FIG. 5. PDOS and simulated STM images at +80 meV of the (9 × 2) phase in the case of (a) a pure DFT calculation; (b) a DFT + U calculation with a value of U = 0.6 eV on Co atoms and U = 10.0 eV on O atoms; (c) a hybrid approach using the B3PW91 xc-functional. The thin black lines in the lower panels indicate the position of the O center row in the models (left) and in the simulated STM images (right).
To test the robustness of the simulated STM pattern with respect to the theoretical approach, we also performed a DFT + U calculation using a value of $U = 0.6$ eV on Co\(^{38}\) (the value for a cation at the interface with a metal support is reduced due to screening effects\(^{20}\)) and $U = 10.0$ eV on O; the latter value has no theoretical background and was chosen as a limit value only to verify whether pushing down the O $p$-states could change qualitatively the STM images (more physically reasonable values of $U$—around 2.0 eV—on O lead to very similar patterns). The result of this calculation is shown in Fig. 5(b): it is evident that the use of $U$ opens a gap in the 3$d$ minority states of Co and stabilizes the 2$p$ band of O by about 2 eV. Nevertheless, the STM simulated image is not qualitatively affected by these changes, as the bright spots still correspond to O atoms. As a final test, we also performed a calculation using the B3PW91 hybrid functional, as it has been shown\(^{39}\) that this xc-functional better describes the electronic structure of transition metal oxides, at the price that the description of the metal support is somewhat deteriorated.\(^{40}\) By looking at the DOS, we can observe the opening of a gap in the 3$d$ band of Co and the fact that the 2$p$ band of O extends in a range between $-7$ and $-1$ eV below the Fermi level. The DOS projected on Pd states is also much reduced at the Fermi energy, as expected from a hybrid approach.\(^{40}\) These remarkable changes, however, do not affect the qualitative features of the STM image, in which the O atoms still appear as bright spots. It is thus possible, but in our opinion unlikely that other xc-functionals, with a more balanced description of the oxide and the metal support,\(^{41}\) will change the predicted STM pattern.

Next, we analyze the effect of the oxide overlayer on the system work function. The work function of the bare metal support, Pd(100), has a value of 5.14 eV according to our DFT/PBE approach, which shifts to 5.21 and 5.31 eV when the c(4 $\times$ 2) and the (9 $\times$ 2) phases, respectively, are deposited on Pd(100). Considering the experimental error bars of $\sim 0.05$ eV, these values compare reasonably well with those drawn from experimental measurements: 5.3 eV for Pd(100), 5.2 eV for the c(4 $\times$ 2) phase, and 5.5 eV for the (9 $\times$ 2) phase, respectively. This provides further support to our structural assignment. The larger value of the work function obtained for the (9 $\times$ 2) phase is in keeping with its more pronounced polar character, and thus its higher surface dipole moment.\(^{42}\) The fact that the value of the work function for both Co oxide phases is not far from that of the bare metal support entails that the reduction in the work function stemming from charge compression is compensated by a charge transfer from the support to the oxide. This can be appreciated in Fig. 6, where isosurfaces of the difference between the electron density of the composite oxide + support system and that of the fragments (separate oxide and support) are plotted at a value of $\pm 0.015$ a.u. In both cases a charge transfer from the metal support to the oxide is apparent, more pronounced in the case of the c(4 $\times$ 2) phase. From a Lowdin analysis of the electron density, one can roughly estimate that an interface Pd atom loses about 0.3 electrons in favor of the oxide slab in the case of the c(4 $\times$ 2) phase, and about 0.1 electrons in the case of the (9 $\times$ 2) phase, respectively.

Finally, the 1D interface boundary between the c(4 $\times$ 2) and (9 $\times$ 2) phases was modeled. To reduce the computational effort to a size compatible with our resources, we focused on the interface between a c(4 $\times$ 2) structure with a square rather than rhombic arrangements of the Co vacancies (note that a shift of the vacancy positions from rhombic to square is observed in the experimental STM images of the boundary, see the dashed rectangles and ellipses in Fig. 3(a)) and a hypothetical (8 $\times$ 2) phase, i.e., a phase in which 14 CoO units are positioned in a (8 $\times$ 2) cell of the support, instead of 16 CoO units in a (9 $\times$ 2) cell as in the (9 $\times$ 2) phase. Replacing the (9 $\times$ 2) cell with the (8 $\times$ 2) cell implies only a minor change in the interatomic distances along the [001] direction (a somewhat larger strain of the oxide layer) but a substantial (more than fourfold) reduction in the size of the system. This leads to a computationally affordable model, shown in Fig. 7, in which each unit cell of the (8 $\times$ 2) phase is matched to two unit cells of the square c(4 $\times$ 2) phase. The STM images simulated after geometry optimization of this model 1D interface are also shown in Fig. 7. It can be seen that the STM pattern of the square c(4$\times$2) structure (from our total energy calculations practically degenerate with its rhombic counterpart) perfectly corresponds to the experimental images of the defects in the c(4 $\times$ 2) phase at the boundary in Fig. 3. It can also be observed that, in contrast to the (9 $\times$ 2) case discussed above, in the simulated STM images of the (8 $\times$ 2) phase protrusions associated with some of the Co ions appear nearly as bright as those associated with the top most oxygens: this is due to a stronger height modulation of the oxygen atoms in
this phase, connected with an increase in the available space, and thus a reduced polar character. Most importantly, a good agreement is found with the experimental STM images of the c(4 × 2)/(9 × 2) interface in Fig. 3. For example, an oxygen atom located at the boundary and belonging to the (8 × 2) cell (highlighted by a cross in Fig. 7) appears as a bright protrusion in the STM image which seems to belong to both phases: it seems to terminate the close-packed Co rows of the c(4 × 2) structure in the [011] direction, but it actually belongs to the row of oxygen protrusions along the [011] direction of the (8 × 2) structure. The bright protrusions highlighted by crosses in Fig. 3(b) can thus be identified as bright oxygen protrusions of the (9 × 2) structure. The theoretical analysis reveals that across the c(4 × 2)/(9 × 2) interface the nature of bright protrusions in the STM changes, from Co atoms imaged bright in the c(4 × 2) phase to O atoms imaged bright in the (9 × 2) phase. This provides a consistent picture of the interfacial region and convincingly supports the structural assignment of both 2D Co oxide phases.

IV. CONCLUSIONS

In the context of oxide nanolayers, CoO x phases represent ideal systems of study as they display the full diversity of these materials, with their complex interplay of chemical, electronic, and mechanical phenomena. The presence of multiple oxidation states, the competition between metal–oxygen, metal–support, and oxygen–support interactions, the charge transfer between oxide layer and metal support, the presence of exotic magnetic phases, the metallization of the oxide film (or in general proximity effects), epitaxial frustration and stress release, and the polar versus nonpolar character of the oxide structure are phenomena that can be quoted in this connection: they all can be found in the CoO x monolayer phases on Pd(100). Being between quasi-noble metal (NiO x ) and transition metal (FeO x ) oxides, CoO x nanolayers exhibit a varied phenomenology, here prototypically exemplified by the competition between a c(4 × 2) and a (9 × 2) coincidence structure. Due to the interplay of a variety of competing interactions the theoretical description of the here discussed CoO x monolayer phases represents a challenging task. The c(4 × 2) structure is homologous to a NiO x /Pd(100) or a MnO x /Pd(100) monolayer 21,22 while the (9 × 2) is similar to a FeO x /Pt(111) monolayer 17—with the noteworthy difference that a polar phase with (111) stacking is realized here on a square-symmetry substrate, such as Pd(100). In the c(4 × 2) phase, the formal oxidation state of Co is +2.67 and one finds an appreciable flow of electron density from the support to the oxide; in the (9 × 2) phase, the formal oxidation state of Co is +2.0 and the charge transfer from the support is much reduced (the charge transfer from the metal support roughly correlates with the formal charge state of the Co atoms). The c(4 × 2) structure is pseudomorphic and basically nonpolar (only a small rumpling), the (9 × 2) is polar but with a wavy structural height modulation. The spin arrangement in the c(4 × 2) is ferromagnetic but with other spin configurations nearly degenerate in energy; in the (9 × 2) an unusual antiferromagnetic phase develops which is predicted to be appreciably more stable than other spin patterns and should in principle be experimentally verifiable. Despite these differences, the two CoO x monolayer phases lie in a narrow range of energy, with the (9 × 2) structure only slightly favored in the experimental preparation conditions with respect to its defective Co3O4 c(4 × 2) competitor, so that the boundary between the two can actually be observed experimentally with unusual clarity, thus confirming (by comparison with a simplified theoretical model) the assignment of which chemical species are imaged in the STM at low bias. The complex balance of these phenomena make the 2D CoO x phases a severe test case for theoretical predictions suggesting that—with the general features of these systems reasonably well ascertained—they can be used to gauge the ability of more advanced theoretical approaches 41 to achieve accurate descriptions.

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