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Nanoscale Patterns on Polar Oxide Surfaces

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Supporting Information

ABSTRACT: Polar ionic surfaces with bulk termination are inherently unstable because of their diverging electrostatic surface energy. Nevertheless, they are frequently observed in nature, mainly because of charge neutralization by adsorbates, but occur also under atomically clean conditions. Several mechanisms have been invoked to explain the stability of atomically clean polar surfaces, but the frequently observed periodic nanoscale pattern formation has not yet been explained. Here we propose that long-range interactions between alternating electropositive and electronegative regions of different surface terminations minimize the electrostatic energy of the surface and thus stabilize the nanoscale pattern. This is illustrated using the example of polar Fe oxide surfaces by combining scanning tunneling microscopy and spectroscopy results with results from density functional theory-based calculations and dipole—dipole interaction models.



■ INTRODUCTION

Oxide surfaces play an important role in many fields of science and technology, for example, in corrosion, electronics, and catalysis, as described in many books and review papers such as refs 1–6. Polar, (partially) ionic oxide surfaces have a diverging surface energy and should be unstable⁷ but are frequently observed, which means that they are charge neutral. For this reason, they have attracted particular attention in an effort to understand the causes of their stability.^{8,9} Iron oxides, mainly hematite (α -Fe₂O₃) and magnetite (Fe₃O₄), have been studied in considerable detail because of their importance in catalysis by noble metals on oxide catalysts.¹⁰⁻¹² The wealth of information about these oxides, which have mixed ionic and covalent bonding, makes them well suited to highlight the surface stabilization mechanism presented here. References 10-12 document extensively the evolution and present state of the understanding of iron oxide surfaces, so that here only aspects relevant to the interpretation and stability of the α - $Fe_2O_3(0001)$ and $Fe_3O_4(111)$ surfaces will be discussed. According to ref 11, the α -Fe₂O₃(0001) surface "seems to remain the most challenging and controversial among the iron oxides", an opinion expressed also in the most recent review,¹ but as will be seen in this work, the same sentiment applies to the $Fe_3O_4(111)$ surface. Both surfaces have frequently been reported with bulk lateral periodicity, usually with oxygen termination. According to density functional theory (DFT) calculations, $^{13-16}$ this termination ("O₃-Fe-Fe"-) of hematite (the last hyphen indicating continuation into the bulk) has the lowest surface free energy at high O₂ chemical potential¹⁴ $\mu_{O,i}$

but on the basis of the ionic model of bulk oxides, it is a polar surface and should therefore be unstable. However, surface atoms are not in their bulk formal oxidation state. Charge transfer between Fe and O atoms and strong atomic relaxation make the surface slab charge neutral and thus stable, but the dipole moment remains large as indicated by the high work function (7.53 eV)¹⁶ of the surface. Similar calculations¹⁷ show that OH termination reduces the surface free energy dramatically irrespective of μ_{O_2} (Figure 6a of ref 17). The surface termination with bulk lateral periodicity will be addressed only briefly in the Supporting Information.

The calculations of relevance here^{13–918} have all been made within the framework of the spin-polarized DFT taking exchange-correlation effects into account in the generalized gradient approximation (GGA), several of them^{15–18} including the strong local Coulomb repulsion between the 3d electrons on the Fe atoms by a Hubbard U term (DFT+U). The DFT+U method requires selection of an effective parameter U, the difference between intra-atomic Coulomb and exchange parameters. U is usually chosen to produce optimal agreement with the properties of the bulk material^{15,16,18} and thus makes these calculations to a certain extent semiempirical. The on-site Coulomb repulsion depends upon the charge and environment of the Fe atom, which is different on and near the surface from that in the bulk, so that U is different for Fe atoms at and near

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the surface. This was taken into account in a first attempt in ref 17. Irrespective of the different approximations, these calculations show a clear tendency of the relative stability of the various individual surface terminations as a function of O₂ chemical potential μ_{O_2} . Low μ_{O_2} values (low oxygen pressures and high temperatures) favor surface termination with Fe, and high μ_{O_2} values favor O termination. For example, GGA calculations for the α -Fe₂O₃(0001) surface without U^{16} predict Fe-O₃-Fe-, O-Fe-O₃- ("ferryl"), and O₃-Fe-Fe- termination with increasing μ_{0} ; those with an effective U of 4 eV predict only the Fe terminations Fe-Fe-O₃- and Fe-O₃-Fe-. With surface-specific values for U_1 the Fe-Fe-O₃termination dominates over an even wider μ_{0} , range.¹⁷ Because of the dependence of the surface termination on U, i.e., on the way on-site correlations on the Fe atoms are taken into account, theory at present cannot make reliable predictions about the surface termination under given experimental conditions. However, it is very useful for the determination of the surface structure of the various possible terminations, their work functions, and electronic and magnetic properties. An important result for the following considerations is the work function, which varies from 3.17 eV for the Fe-Fe-O3termination to 8.51 eV for the O₃-Fe-Fe- termination. The first value is much lower than the work function of Fe of \approx 4.7 eV, indicating a significant positive dipole moment, while the high second value implies a large negative dipole moment. A surface with either one of these terminations has therefore a considerable electrostatic energy.

The electrostatic energy can be reduced by long-range dipole-dipole interactions when the surface is broken up into regions with opposite dipole moments, whose surface energy is determined by short-range interactions. Phenomenological treatments of the competition between long-range and shortrange interactions have been around for a long time and used to describe systems such as Langmuir monolayers on water, thin ferromagnetic films with perpendicular magnetization, misfitting monolayers, or phase segregation on surfaces involving various long-range interactions. The interaction of relevance in the present system is the dipole-dipole interaction between regions with different work functions. Calculations for twocomponent systems (two different work functions, Φ_{A} and Φ_{B}) show that their ground state consists of periodic structures of domains differing in their work functions.^{19,20} When the areal fraction of one of the components is lower than 0.286 or higher than 0.714, the ground state is a hexagonal phase, consisting of nearly circular regions with work function Φ_A imbedded in a background with work function $\Phi_{\rm B}$ and vice versa. Between these values, a striped phase is the ground state. These calculations assumed that the boundary energy between the two phases is independent of orientation, i.e., a noncrystalline substrate. A similar energy minimization has to be expected on oxides with surfaces, which have terminations differing in work function. However, the 6-fold $[\alpha$ -Fe₂O₃(0001)] or 3-fold $[Fe_3O_4(111)]$ substrate and the existence of several work functions make the ground states more complex. The coexistence of Fe- and O3-terminated regions has actually been suggested in the DFT calculations¹³ based on their low surface energy (but not on the dipole-dipole interaction influence on the surface order) and demonstrated experimentally by scanning tunneling microscopy (STM), both in ultrahigh vacuum $(UHV)^{13,21}$ and in H_2O .²² More recently, GGA+U calculations¹⁸ actually have shown that already

combining two Fe-terminated and two O-terminated surface regions in a 4×4 unit cell is energetically more favorable than the sum of the individual terminations.

Long-range order of two domains has been observed by STM on α -Fe₂O₃(0001), called "biphase" ordering, ^{23,24} and has been attributed to the coexistence of α -Fe₂O₃(0001) and FeO(111) islands. This long-range order produces a "floreted" or "rosette" superstructure low-energy electron diffraction (LEED) pattern that had been reported previously²⁵⁻²⁷ but was interpreted by double scattering between an $Fe_3O_4(111)$ overlayer and the α -Fe₂O₃(0001) substrate, an interpretation also adopted in a later study.²⁸ In more recent low-energy electron microscopy (LEEM) studies of surface reactions on the α -Fe₂O₃(0001) surface²⁹ and of the α -Fe₂O₃ \leftrightarrow Fe₃O₄ surface phase transition,^{30,31} this LEED pattern has become the signature of the α -Fe₂O₃(0001) surface. Long-range superstructures occur also on the $Fe_3O_4(111)$ surface.³²⁻³⁷ In the first study³² of this surface, the STM images were interpreted in a manner similar to those of the α -Fe₂O₃(0001) surfaces^{22,23} as consisting of $Fe_3O_4(111)$ and $Fe_{1-x}O(111)$ islands without explaining the cause of the long-range order. An attempt at such an explanation was made later³⁴ in terms of localized polarons or a charge density wave, an explanation that, however, was repudiated convincingly.³⁷ Thus, there is at present no explanation of the long-range order, neither for the α -Fe₂O₃(0001) surface nor for the Fe₃O₄(111) surface. In this paper, we combine the results of DFT calculations of the shortrange interactions with the idea of dipole-dipole interactioncaused long-range interactions to show that the STM and LEED results obtained in this work and in previous studies can be explained in a very natural manner.

METHODS

The DFT-based theoretical calculations utilize a plane wave basis to represent solutions of the Kohn-Sham equations and the projectoraugmented wave (PAW) method³⁸ to describe the electron-ion core interactions as implemented in the VASP code.^{39,40} We employ the generalized gradient approximation (GGA)^{41,42} and apply a Hubbard U correction (GGA+U) to treat the correlated Fe 3d electrons. The calculations applied the rotationally invariant approach of Dudarev et al.⁴³ with an effective parameter U. Throughout this work, U represents the effective parameter of interaction between electrons, i.e., the difference between the Coulomb and exchange parameters. For the Fe 3d states in magnetite and hematite, we employ U values of 3.61 and 4.0 eV, respectively. Surface-specific values¹⁷ of U for the Fe- $\mathrm{Fe-O_{3}-}$ termination of hematite were also applied. The plane wave basis energy cutoff was set to 500 eV, and the surface Brillouin zone was sampled using a Γ -centered 6 \times 6 \times 1 k-point mesh with a Gaussian broadening of 0.1 eV. The surfaces were modeled by symmetric slabs and a 1 \times 1 surface unit cell. The Fe-terminated α - $Fe_2O_3(0001)$ slab was built of 18 atomic layers (12 Fe and 6 O layers), whereas the slab representing the Fe_{tet1} -terminated $Fe_3O_4(111)$ surface consisted of 29 (19 Fe and 10 O) atomic layers. The details about slabs applied to represent other terminations are given in refs 16 and 44. All systems were structurally optimized according to the Hellman-Feynman forces with the positions of all atoms fully unconstrained. The work function was calculated as the difference between the electrostatic potential energy in the vacuum region and the Fermi energy of the slab. The magnetic moments were also calculated for both the α -Fe₂O₃(0001) surface and the Fe₃O₄(111) surface (refs 16 and 44) but are not discussed in the following because they are irrelevant in the context of this paper.

The STM and LEED studies were performed in two Omicron systems [one in Berlin (I) and the other in Poznań (II)]. The TPD experiments were conducted in system I and the STS and dI/dV mapping in system II. After baking at 150 (I) and 120 °C (II), a base



Figure 1. Surface energies of various relaxed α -Fe₂O₃(0001) surface terminations as a function of oxygen chemical potential μ_{O_2} using the same computational procedures but with different Hubbard effective U^d and U^p terms correcting for Fe 3d and O on-site electron correlations: (a) $U^d = 0$, (b) $U^d = 3.81$, (c) U^d surface-specific, and (d) U^d surface-specific, where $U^p = 5.9$ eV. The surface-specific values are from Table 3 of ref 17. The curves in panel b are indistinguishable from those in ref 16, where $U^d = 4$ eV. Dashed lines show the Perdew–Wang (PW91) exchange-correlation functional, and solid lines show the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional (for only the Fe–O₃–Fe–, Fe–Fe–O₃–, O₃–Fe–Fe–, and O₁–Fe–Fe– terminations). The vertical lines mark the range of accessible oxygen chemical potential.

pressure of 2×10^{-10} mbar could be achieved in system I, whereas in system II, it was 5×10^{-10} mbar in the main chamber and 3×10^{-11} mbar in the STM chamber. Iron oxide films were grown on Pt(111) single crystals of 99.995% (I) and 99.999% (II) purity by cycles of Fe deposition at room temperature and annealing at elevated temperatures in O2 as described in Table S3. Iron was deposited from electron bombardment-heated 99.95% (I) and 99.995% (II) 2 mm diameter Fe rods at angles of incidences of $\approx 45^{\circ}$ (I) and $\approx 90^{\circ}$ (II). The Fe deposition rates, determined by deposition of submonolayer amounts of Fe onto clean Pt(111) and measurement of the coverage with STM, were 1 (I) and 0.07 ML/min (II). During oxide film preparation, the pressure was in the low 10⁻⁹ mbar range. The first layer [FeO(111)] served as a blocking layer against diffusion of Fe into the substrate during the second deposition and oxidation. For the growth of α -Fe₂O₃, a higher pressure and a higher temperature were used to achieve thorough oxidation, with increasing pressure and temperature to improve good long-range order. The low initial temperature was used to minimize the tendency for three-dimensional growth. Fe₃O₄ layers required a much lower pressure during oxidation to prevent α -Fe₂O₃ formation, and excellent long-range order was obtained already at 880 K. Initial cleaning of Pt crystals was performed by extensive cycles of sputtering with 1 keV $\mathrm{Ar}^{\scriptscriptstyle +}$ ions, annealing in O_2 at 800-1000 K, and annealing for 5-10 min at 1300 K in UHV. The two gases, Ar and O₂, were >99.9% (I) and 99.999% (II) pure. Highpurity water used in the high-pressure oxidation studies was cleaned by pumping during multiple freeze-thaw cycles in liquid nitrogen vapor. The deposition of Fe onto the oxide films was performed in the same

manner as during oxide growth but with a rate of ≈ 3 ML/min. Au, 99.95% pure, was deposited from a crucible at a rate of ~0.4 ML/min, as determined by STM of submonolayer Au deposited onto Fe₃O₄(111). During deposition of the two metals, the pressure stayed in the 10⁻¹⁰ mbar range. All STM measurements were performed at room temperature in constant current mode with different bias voltages, using commercial Pt₈₀Ir₂₀ (I) and W tips (II). Scanning tunneling spectroscopy (STS) and dI/dV mapping measurements were taken using a lock-in amplifier with a modulation voltage of 40 mV. TPD studies were performed with a heating rate of 3 K/s.

RESULTS AND DISCUSSION

The various calculations mentioned in the Introduction show considerable differences between the relative surface energies. These calculations differ not only in the manner in which Fe and O on-site correlations have been taken into account but also in computational details such as energy cutoff, k point mesh, and convergence of forces during energy minimization. This makes a comparison of their results difficult. Therefore, we recomputed various terminations with different on-site correlations but with the same computational procedures. The "phase diagrams" of four selected cases are shown in Figure 1.

The following results are the most striking. (i) The O_3 -Fe-Fe- termination has a low surface energy only if on-site

Table 1. Work Function	(in electronvolts) of Relaxed	(Unrelaxed)) α -Fe ₂ O ₃ ((0001) Surface Tei	minations ⁴
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exchange correlation	Fe-C	D ₃ -Fe-	Fe-F	e-O ₃ -	O ₃ -H	Fe-Fe-	0 ₁ –H	Fe-Fe-
PBE	4.15	(3.31)	3.63	(4.09)	7.44	(8.31)	5.91	(5.71)
PBE+4.0	4.69	(2.79)	3.17	(3.88)	8.40	(8.82)	6.16	(6.29)
PBE+3.81	4.61	(2.78)	2.88	(3.85)	8.39	(8.82)	6.19	(6.31)
PBE+3.81+U ^p 5.9	4.65	(2.90)	2.88	(3.86)	7.60	(7.96)	6.20	(4.85)
$PBE+U^{d}_{ss}$	4.76	(2.73)	2.85	(3.92)	8.71	(8.81)	6.27	(6.32)
$PBE+U^{d}_{ss}+U^{p}5.9$	4.68	(2.84)	2.85	(3.89)	8.20	(8.00)	5.35	(4.87)
^{<i>a</i>} PBE+4.0 denotes PBE+ <i>U</i>	with an effecti	ve <i>U</i> of 4.0 eV.	U ^d ss denotes su	rface-specific val	ue of U^{d} with t	he U^{d} and U^{p} va	lues for oxyger	n p states, taker

TBE+4.0 denotes PBE+U with an effective U of 4.0 eV. U_{ss}^{-} denotes surface-specific value of U⁻ with the U⁻ and U⁺ values for oxygen p states, taken from ref 17.

correlations are neglected (Figure 1a). (ii) When a fixed effective U^d value of 3.81 or 4 eV is used for all Fe atoms in the surface layer, then the Fe-O₃-Fe- termination has the lowest energy over the whole μ_{O_2} range (Figure 1b). (iii) When surface-specific Fe 3d on-site correlations U^{d} are used, the choice of the exchange-correlation functional becomes critical: the surface energy of the Fe-O₃-Fe- termination becomes so high with the GGA-PBE functional that this termination should not appear over the complete accessible μ_{O_2} range (Figure 1c,d). Inclusion of fixed O on-site correlations U^p (Figure 1d) does not change these tendencies much. The surface density of states shows that all surfaces have become metallic after relaxation. The work functions of the main terminations calculated here in the relaxed and unrelaxed states, using neutral, symmetric slabs, are compiled in Table 1 and 2 for hematite and magnetite, respectively. In Tables S1 and S2, they are compared with literature values.

Table 2. Work Functions of Relaxed and Unrelaxed $Fe_3O_4(111)$ Surfaces Calculated with PW91+U (U = 3.61 eV)

	work function (eV)			
termination	relaxed	unrelaxed		
Fe _{tet1}	5.49	3.20		
O1	7.91	9.15		
Fe _{oct1} (Kagome)	4.06	4.12		
O2	7.54	8.80		
Fe _{tet2}	4.20	4.01		
Fe _{oct2}	3.00	4.02		
Kagome+Fe	4.48	4.74		
ferryl	7.63			

As expected, the relative displacements of the O and Fe planes during relaxation increase the work function of the Fe-O₃-Fe- terminated surface from highly electropositive values (as found, for example, on alkali surfaces) to higher values. However, the work functions are still significantly smaller than those of the relaxed O-terminated surfaces, providing enough driving force for dipole-dipole interaction-driven long-range order. On the Fe-Fe-O₃- terminated surface, relaxation decreases the work function. This is somewhat surprising because relaxation shifts the neighboring Fe and O layers toward each other, which would suggest an increase in the work function. However, the decrease becomes clear by noticing that the shrinking of the separation of the $Fe-O_3$ layers is nearly perfectly canceled by the expansion of the Fe-Fe separation of the outermost Fe layer. The expansion of the O_3 -Fe distance shifts the whole Fe-Fe-O3- trilayer outward from the underlying Fe layers (cf. Figure 3 of ref 16), thus producing

a decrease in the work function. Inspection of Table S1 shows that the work function changes upon relaxation depend very little on the specific parameters used in the calculations. Therefore, they can be reliably used in the discussion of the dipole-dipole interactions despite the strong changes in the surface energies in Figure 1 with the computational parameters.

Turning to the long-range order seen in experiments, we note that Figure 2 shows a typical topography (a) and current (b) STM image of the "biphase" α -Fe₂O₃(0001) surface, the Fourier transform (c), and the LEED pattern (d) of a larger area. The period of the superstructure deduced from the FFT, 4.2 nm, agrees very well with that obtained from the LEED pattern and with those from previous studies. Three areas in the superstructure unit cell, differing in periodicity and contrast, marked α , β , and γ for comparison with earlier work,^{23,24} are seen.

The STS spectra (Figure 3) of these regions show a wide bias range without tunneling current caused by the band gap of ≈ 2 eV (indicated by the vertical lines), which limits the bias range for imaging. This is in particular evident in the "hole" region γ , while in the α and β regions, states near the band edges allow tunneling also in the band gap. It should be noted that the "hole" is much larger than in the earlier images of the "biphase", which were obtained by reducing a bulk α -Fe₂O₃(0001) surface.^{23,24} This is not surprising because the relative size of the three regions was found to depend strongly on the oxidation conditions (O₂ pressure and temperature) and, when starting from a (1×1) surface, upon the reduction conditions. For a given surface condition, the image depends of course also upon bias voltage and tip condition because the densities of states involved in tunneling depend upon bias voltage and tip condition. While the relative size of the three areas in the unit cell depends upon the oxidation-reduction conditions, the lattice constant of the long-range order is determined by the interplay of domain boundary energy and dipolar coupling ⁶⁰ The observation that the lattice constant of the energy.² superstructure is independent of the relative size of the three domains suggests strong coupling between these two quantities.

Images from larger surface regions give better insight into the long-range order, the influence of steps, and the relationship between different terraces. Figure 4 shows a topography (a) and a density of states (b) image taken with a tungsten tip at a bias voltage of +2.0 eV. The surface was not completely clean as seen by the white spots in the "hole" regions in panel a. While some of the deviations from a regular honeycomb lattice can be attributed to sample drift, some of them are clearly caused by imperfections in the surface order such as the direction of the long-range order indicated by black lines in panel a. The density of states shows a pronounced maximum in the γ ("hole") region, indicating tunneling into the unoccupied Fe 3d states.



Figure 2. Typical α -Fe₂O₃(0001) surface annealed several times at 1000 K. (a) STM topography image taken with a +2.0 V bias and a 1.0 nA current using a W tip. [Positive bias means tunneling into the unoccupied states (Fe 3d) of the sample.] The regions with different surface terminations are marked. (b) STM current image of the area shown in panel a. (c) Fast Fourier transform (FFT) of a single terrace region. The FFT of panel a was dominated by the spatial frequencies of the atomic distances in the image; for this reason, the FFT presented in panel c was taken from another STM image without atomic resolution. (d) LEED pattern (64 eV) of a larger region that includes terraces with rotated long-range order.



Figure 3. STS spectra of the regions marked in Figure 2a taken with a W tip: α (green), β (red), and γ (black).



Figure 4. Large-scale STM images of an α -Fe₂O₃(0001) surface. (a) Topography image. The lines indicate deviations from the long-range order. (b) Density of states image (d*I*/d*V* map). Bias of +1.5 V, current of 1.0 nA, W tip.

Enhanced tunneling occurs also along the steps. Larger scan areas (Figure 5) reveal the relationship between different terraces. Most of them are separated by 0.23 nm ("1 ML") high steps and some by 0.47 nm ("2 ML") high steps, corresponding to one-sixth and one-third of the *c* axis of the hexagonal unit cell, respectively. While the direction of the superlattice on terraces separated by 2 ML steps is the same, it is rotated between terraces separated by 1 ML steps. This is indicated by the lines in Figure 5a, by the Fourier transform of the image (Figure 5c), and is also seen in the LEED patterns. Analysis of many data results in a rotation angle of $20 \pm 2^{\circ}$. The origin of this rotation is not clear, but it is interesting to note that the spins of the Fe atoms in the two terraces separated by 2 ML high steps.

Returning to the superstructure unit meshes seen in Figures 2a and 6, we note it is evident that they do not consist of two but three phases (α , β , and γ). Their nature can be identified by comparison to the detailed DFT calculations. When an arbitrary limit for the surface energy of 100 meV/Å² is set in Figure 1, many terminations are possible in the accessible μ_{O_2} range: Fe–Fe–O₃–, Fe–O₃–Fe–, ferryl, O₁–Fe–Fe–, O₂– Fe–Fe–, or O₃–Fe–Fe–. This makes reliable identification difficult. The work functions of these terminations range from 2.85 to 8.71 eV (Table 1 and Table S1). These large differences favor minimization of the electrostatic energy by formation of periodic domains with large work function differences as mentioned above. The unit meshes of the superstructure show in the γ region \approx 0.5 nm periodicity (see Figures 2a and 6).



Figure 5. (a) Large-scale STM image of an α -Fe₂O₃(0001) surface showing the typical multiterrace structure with rotations of the superstructure direction indicated by tilted white lines. The height differences between the terraces along the horizontal white line are plotted in panel b. (c) FFT of panel a showing the rotation between monolayer terraces. Bias of +2.0 V, current of 0.7 nA, W tip.



Figure 6. STM images of an α -Fe₂O₃(0001) surface showing various atomic periods in the γ region under different tunneling conditions. (a) Sum of topography and current images of a two-terrace region showing the 0.3 nm period in the center of the γ region, marked by white circles, taken at +1.4 V bias and 0.7 nA current. (b and c) Current images of terraces on different films, taken with -2.0 V and 0.7 nA and 2.0 V and 2.0 nA, respectively. The circles in panel c indicate the α regions, topped by triangles, and the dots the β regions. All images were taken with a PtIr tip.

Three of the surrounding regions (α) have ≈ 0.5 nm periodicity, and the other three regions (β), alternating with the α regions,

≈0.3 nm periodicity, but frequently, no atomic resolution could be obtained. Simulated STM images using the Tersoff– Hamann approximation⁴⁵ suggest that the α region is O– Fe–O₃–(ferryl) terminated and the β region Fe–O₃–Fe– terminated.

The atomic distances in the γ region are, however, not compatible with O₃-Fe-Fe- termination, which is deduced from metal adsorption studies discussed below. A possible explanation is that the tunneling is dominated by the Fe atoms below the O₃ layer. This possibility is suggested by the high density of states in the holes seen in Figure 4b, where tunneling into unoccupied Fe 3d states occurs. In fact, under some tunneling conditions, the 0.3 nm periodicity of the O₃ layer is visible in the center region (Figure 6a). In general, however, only the 0.5 nm distance pattern, expected for an O₁-Fe-Fetermination, is found in the γ region (Figure 6b,c). Panels b and c of Figure 6 have been obtained with opposite bias polarities from different terraces, which expose different cuts of the unit cell at the surface as mentioned above (Figure 5). It is interesting to note that in Figure 6b in most of the α (ferryl) regions the 0.5 nm spacing is replaced by triangles with internal 0.3 nm spacing (Figure 2a), the same spacing as in the β region. It appears that the oxygen of the ferryl layer is replaced by a Fe layer similar to the Fe termination in the β region.

Whether the tunneling polarity or the surface cut is responsible for the differences between panels b and c of Figure 6 is not clear. This example, however, shows that much more detailed studies are needed before a deeper understanding of the nature of the termination of the three regions as a function of the surface cut can be achieved. Furthermore, while the Tersoff-Hamann approach provides a fundamental understanding of the tunneling process, which might be adequate for simple metal surfaces, it does not cover the complexities of surfaces consisting of (partially) positively and negatively charged atoms and strongly localized 3d electrons. More sophisticated STM image simulation models such as those described in ref 46 will be necessary to describe such systems. Work along this line is in progress. An additional complication is the strong work function variation across the surface. For example, clear boundary effects are seen in the γ region: the contrast decreases with an increasing distance from the boundary, giving the impression of three domains (Figures 1a and 6c). The atomic rows in the resulting triangular pattern are lined up approximately parallel to the γ boundaries, at which the work function difference is high. Apparently, the strong potential gradient between the α and γ regions caused by the work function difference has a strong influence on the tunneling behavior. For a sharp $\alpha - \gamma$ boundary, the field is approximately 4 V/0.3 nm, which is comparable with the field between the tip and sample on the order of 1 V/0.1 nm.

Keeping all these effects in mind, we must consider the assignment of the various regions in the STM images to specific terminations in this study and previous studies of Fe oxides to be very tentative. Similarly, the difficulty in the theory of taking site-dependent on-site 3d electron-correlation effects into account correctly with proper *U* and the limitations of the Tersoff–Hamann approximation for simulating STM images of complex surfaces at present make an unambiguous determination of the local termination difficult. A more reliable method is to make use of the different adsorption energies on different surfaces. GGA+*U* calculations of the adsorption of single Au, Pd,¹⁶ and Fe⁴⁷ atoms show that their energies of binding to the O₃–Fe–Fe– termination are by factors of 3–4 higher than

those for binding to the $Fe-O_3-Fe-$ termination. Deposition of these atoms allows therefore a clear distinction between these two surfaces.

Figure 7 shows the topography (a) and current (b) STM image of an α -Fe₂O₃(0001) layer on which a small amount of



Figure 7. STM topography (a) and current (b) images of an α -Fe₂O₃(0001) surface with a low coverage of Au deposited at 300 K. The blue circles indicate empty γ regions, the yellow circles γ regions filled with chemisorbed Au islands, and the white circles triangles on the α regions. In Figure S1, the black enclosed region in panel b is shown at a higher magnification. Bias of +1.4 V, current of 0.7 nA, PtIr tip.

Au has been deposited. In the topography image, many of the γ regions of the long-range order pattern of the surface are filled with diffuse regions and many with bright particles, which a profile analysis shows to be ≈ 0.25 and ≈ 0.5 nm high, respectively, suggesting Au single- and double-layer particles. No changes are seen outside these regions, indicating that Au has condensed only in the γ regions. The current image (Figure 7b and Figure S2) shows in the dark γ regions the atomic details of the clean surface with 0.5 nm spacing and in the diffuse γ regions either a periodic structure with 0.6 nm periodicity, very noisy features, or streaking in the scanning direction. The first structure does not fill the γ regions completely and can be attributed to single chemisorbed atoms. Their spacing is larger than the substrate spacing because of the strong repulsion between the Au atoms, which carry a charge of +1e.⁴⁸ The repulsion limits also the size of the chemisorbed regions because the adsorbed Au⁺ is increasingly displaced from the strong bonding sites so that the layer becomes unstable with an increase in size. The tip then can easily destroy the layer, causing the noisy features, or pull the adsorbate along, causing the streaking. It is unlikely that Au, clusters form because the binding energy per atom decreases with an increase in *n*, at least up to n = 4.⁴⁸ Rather nanocrystals form with an increasing number of Au atoms in γ regions as seen in Figure 7. The preferential condensation is even more visible when several Au monolayers have been deposited as seen in Figure 8.

There is some disorder, but the long-range order is locally still well pronounced even after annealing at 700 K. The Au 1.0–1.2 nm thick nanocrystals are nearly exclusively located in the γ regions, which is evident in places where some of them were removed by the STM tip, revealing their location (see Figure S3).

Fe adsorption is predicted by theory⁴⁷ also to be strongest on the O₃-terminated surface. The experiment shows adsorption at very low coverages only in the γ regions as seen in Figure 9a. However, the two-dimensional adsorption seen in the case of Au (Figure 7) has not been observed for Fe. Instead, several small islands form with increasing coverage in the γ regions (Figure 9a). A similar STM image has been reported for the surface of an α -Fe₂O₃(0001) crystal, which had been reduced



Figure 8. STM topography images of an α -Fe₂O₃(0001) surface with a high coverage of Au deposited at 300 K (a) and annealed at 700 K (b). An enlarged edge of such a layer is shown in Figure S3. Bias of +2.0 V, current of 0.7 nA, PtIr tip.



Figure 9. STM topography images of an α -Fe₂O₃(0001) surface with very low (a) and high (b) Fe coverage deposited at 450 and 400 K, respectively. Bias of +2.0 V, current of 0.7 nA, PtIr tip.

strongly and had been partially reoxidized, but the features in the holes were attributed to purely electronic effects.⁴⁹ With a further increase in Fe coverage, the number of islands in the γ region increases only slightly (Figure 10a) and larger nanocrystals form outside these regions but only in the α (ferryl) regions as indicated by the circle in Figure 10b (see also Figure S4).



Figure 10. STM topography images of an α -Fe₂O₃(0001) surface covered with a low (a) and intermediate (b) amount of Fe deposited at 300 K. In panel a, Fe is found nearly exclusively in γ regions, and in panel b, many Fe particles grow on the α regions as indicated by the circle. Bias of +2.0 V and current of 3.0 nA (a) and bias of +2.0 V and current of 0.7 nA (b). Both images taken using a PtIr tip. Figure S3 shows more details of the low surface coverage.

No Fe adsorption is seen on the Fe-terminated (β) regions. This agrees with calculations, which show a much weaker bonding of monomers on the Fe termination than on the oxygen termination (γ region) at low coverage (2.93 eV vs 8.3 eV).⁴⁷ For Fe adsorption on the ferryl termination, no calculations are available for comparison. At even higher coverages (several monolayers) and slightly elevated temperatures, which allows better surface diffusion, the same self-organization pattern is seen as in the case of Au, but now the Fe nanocrystals are not on the γ region but are located on the α (ferryl) regions (Figure 9b and Figure S5). Thus, while self-



Figure 11. STM images of a $Fe_3O_4(111)$ surface. (a) Topography, (b) current image, and (c) enlarged current image showing the three regions usually present with oxidation state-dependent ratios. Bias of +1.0 V, current of 1.14 nA, PtIr tip, FFT-filtered.

organization is determined by the long-range periodicity of the substrate, the location of the self-organized nanocrystals is determined by the short-range chemistry. These adsorption results clearly allow distinction between O- and Fe-terminated regions, information that could not be deduced reliably from the geometry of the STM images of the clean surface due to the limitations of the theory mentioned above.

In contrast to α -Fe₂O₃(0001), which has a band gap of ≈ 2 eV, $Fe_3O_4(111)$ is half-metallic. This allows imaging over a wide tunneling bias range as illustrated in ref 50. The superstructures on the $Fe_3O_4(111)$ surface have unit cells whose composition seems to depend more on the preparation method than for those on the α -Fe₂O₃(0001) surface. This is clearly evident in earlier studies, which interpreted the unit cell composition in different ways.³²⁻³⁷ No cause of the long-range order was given, except one proposal,34 which, however, has been clearly repudiated.³⁷ As in the case of the α -Fe₂O₃(0001) surface, the combination of short-range interactions and work function difference-induced long-range interactions provides a natural explanation of the superstructures. The $Fe_3O_4(111)$ surface can in principle have eight terminations. The structure, energetics, and properties of the most stable ones have been calculated with the same methods used for the α -Fe₂O₃(0001) surface.^{44,51–54} With increasing oxygen chemical potential $\mu_{0,i}$ the most stable terminations are found to be the Fe_{oct2} , Fe_{tet1} , O_1 , and O_2 terminations,^{44,51-54} with the ferryl termination at intermediate oxidation states.⁵⁴ The "phase diagram" calculated in this study is shown in Figure S5. The Fe and O terminations show large work function differences similar to those mentioned above for the α -Fe₂O₃(0001) surface, so that the total energy of the $Fe_3O_4(111)$ surface will be reduced by work function difference-mediated long-range order. For example, earlier calculations gave for the $\mathrm{Fe}_{\mathrm{oct2}}$ termination a work function of 3.90 eV, the O_1 termination 8.09 eV,⁴⁴ and the ferryl termination 7.61 eV.⁵⁴ These values are in good qualitative agreement with those calculated here (Table 2) as a more

detailed comparison with previously published data (Table S2) shows.

The relative contributions of the various surface terminations are expected to depend upon the oxidation-reduction conditions, which is clearly seen in the range of observed superstructures reported previously³²⁻³⁷ and illustrated for our own work in Figure S6. The increase in the region with the 0.6 nm spaced structure has been attributed to an increasing level of oxidation³² or to an increasing level of reduction.³⁷ A distinction between these two interpretations can be made on the basis of theory, which predicts increasing O₁ and O₂ termination with increasing oxygen chemical potential.^{44,51,54}

The details of the composition of the unit cells are shown in Figure 11 with the nomenclature used in the first highresolution STM study of the Fe₃O₄(111) surface for comparison. The size of the χ region decreases with a decrease in μ_{O_2} (Figure S6 and refs 32 and 37). On the basis of theory, the χ region therefore must be assigned to O_1 or O_2 termination, although the image does not agree with a Tersoff-Hamann level simulation, another example of its failure. Simultaneously, the surrounding θ and φ regions grow until at the lowest μ_{O_2} conditions studied only these two regions are left. This suggests that the θ region is terminated by O and Fe, probably ferryl, while the φ region consists only of Fe with a dense, 0.3 nm spaced packing, a configuration that has not been considered in the published calculations. This packing density does not exist in the bulk of Fe₃O₄ but corresponds to that of Fe(111) layers in FeO. This, however, does not imply that the superstructure consists of interconnected FeO and Fe₃O₄ islands but shows only that the loss of oxygen leads to a Fe-rich surface layer such as the Kagome +Fe layer in Table 2.

In principle, a more reliable estimate of the surface termination could be obtained as in the case of the α -Fe₂O₃(0001) surface by making use of the different binding energies on different terminations. DFT calculations with the methods used in the calculation of the surface structure of the

clean surface actually have been performed for Au,^{44,55,56} Fe,⁴⁷ and several other transition and noble metals,⁵⁶ and they do show significant differences between the binding energies on different surface terminations. An earlier study⁵⁰ clearly shows a regular array of Fe and Cr clusters on the 5.0 nm superstructure on this surface, which indicates a variation of the binding energy with surface termination, but the location of the clusters in the unit cells was not determined.

CONCLUSIONS

Oxide surfaces, which have at least two surface terminations with comparable surface energies and different work functions, can minimize their total energy by forming long-range superlattices. We illustrated this here for two iron oxide surfaces by combining experimental results with results of DFT calculations of short-range interactions and the principles of dipolar long-range interactions. The two surfaces have a common building block consisting of a central oxygenterminated region surrounded by three Fe and three mixed Fe–O regions in a cyclical arrangement. The ratio of the α - $Fe_2O_3(0001)$ and $Fe_3O_4(111)$ superstructure unit cell dimensions is identical to that of the elementary twodimensional unit cell dimensions of the two oxides. The size of the oxygen-terminated region increases with oxygen chemical potential at the expense of the surrounding regions. Energy minimization by superlattice formation and energy minimization by relaxation of individual surface terminations are probably not independent processes; superlattice formation may well reduce the driving force for relaxation of the participating surface terminations in the absence of dipoledipole interactions.

Superlattice formation should occur also on other surfaces with competing short- and long-range interactions and large differences between the work functions of different terminations. Quantification of this phenomenon will require extension of the long-range interaction theory to more than two phases and crystalline substrates, improvement of the description of the on-site Coulomb interactions,⁵⁷ development of the theory of tunneling for the comparison of STM images between theory and experiment, and, equally importantly, development of experimental procedures for quantitative control of the oxygen chemical potential. It is hoped that this study will stimulate work along these lines.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.6b03040.

Additional tables with work functions of different surface terminations and figures on the characterization of materials and comments on the α -Fe₂O₃(0001)-(1 × 1) structure (PDF)

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Author Contributions

M.L., I.M.N.G., and Z.-H.Q. performed the experiments. E.B. conceived the project and wrote the manuscript with support from A.P., M.L., and A.K. T.O., T.P., and A.K. performed and analyzed the theoretical calculations. S.S. and H.-J.F. in addition to all other authors contributed to the discussions. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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