Thermodynamic stability and atomic and electronic structure of reduced Fe₃O₄ (111) single-crystal surfaces

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Magnetite (111) single-crystal surfaces prepared in situ under different reducing conditions and—as a result—with varying stoichiometries have been studied by scanning tunneling microscopy, low-energy electron diffraction, and x-ray photoemission spectroscopy. The coexistence of several surface structures has been detected, indicating only small differences in their relative stabilities. In particular, an unusual previously unreported superstructure has been found for a strongly reduced surface. Its microscopic origin is discussed against the background of recent results from scanning tunneling microscopy of the oxidized magnetite (111) surface and from ab initio thermodynamics. Partly at variance with and partly complementary to these results, we regard as driving force elastic strain due to the lateral mismatch between Fe$_3$O$_4$ substrate and Fe$_{1-x}$O-like overlayer.

I. INTRODUCTION

Magnetite, Fe$_3$O$_4$, has recently evoked great interest due to its high potential for applications in magnetoelectronics. It has been predicted to be a half-metallic ferromagnet yielding a complete spin polarization at the Fermi level. In contrast, spin-polarized photoemission studies found the polarization of Fe$^{3+}$ cations occupy 8 of the 64 available tetrahedral interstitials. The stacking sequence of oxygen layers and the eight Fe$^{2+}$ cations resides in 16 of the 32 available octahedral interstitials. The stacking sequence of magnetite along the crystal direction [111]. Side view from direction [121], ionic radii are scaled down, and six possible bulk terminations are indicated: oxygen terminations O$_1$ and O$_2$, (in bulk) tetrahedrally coordinated iron terminations Fe$_{oct1}$ and Fe$_{oct2}$, and (in bulk) octahedrally coordinated iron terminations Fe$_{oct1}$ and Fe$_{oct2}$.
because they are highly sensitive not only to the particular experimental preparation conditions but also to the entire thermochemical history.

Zhu et al. have recently compiled a phase diagram for the \( \text{Fe}_3\text{O}_4 \) (111) surface using first principles thermodynamics and compared the relative stability of five bulk terminations in contact with an oxygen reservoir.\(^7\) As expected, the stability of different atomic configurations of the polar (111) surface varies upon changing the surface stoichiometry. Their calculations reveal that under low oxygen partial pressures, the Fe-terminated surfaces are more stable, while in the oxygen-rich regime, the \( \text{O}_1 \) termination is energetically favored. The predicted most stable surface configurations, i.e., terminations by \( \text{Fe}_{\text{tet}} \), \( \text{Fe}_{\text{oct}} \), or \( \text{O}_1 \) layers, exhibit metallic properties at variance with the results from ultraviolet photoemission.\(^7\)

Several experimental studies of the \( \text{Fe}_3\text{O}_4 \) (111) surface are available up to now. They divide into investigations of magnetite (111) films grown on Pt(111) (Refs. \(8\)–\(10\)) and studies of single crystals.\(^8\) In this work, we report on systematic investigations of thermally prepared synthetic single-crystal surfaces as prepared under reducing conditions.

II. EXPERIMENT

Experiments were performed in an ultrahigh vacuum (UHV) system with a base pressure in the low \(10^{-10}\) mbar regime. The surface analysis chamber is equipped with both a scanning tunneling microscope (VT STM, Omicron Nanotechnology) and a photoemission spectrometer (EA 125 HR, Omicron Nanotechnology), while the preparation chamber is furnished with a sputter gun, a homebuilt heating station, and a gas inlet system for oxygen of ultrahigh purity (99.9999%). Temperature was measured \textit{ex situ} with a focusing infrared pyrometer.

Synthetic single-crystalline magnetite was grown by means of a floating zone technique in a mirror furnace. Samples were cut with a thickness of 3 mm and a surface area of about 10 mm\(^2\) from the obtained rods. The \textit{ex situ} surface preparation consisted of lapping (SiC paste, grain size \(\sim 3\) \(\mu\)m), polishing, and cleaning in an ultrasonic bath with organic solvents. The standard \textit{in situ} cleaning comprised 1 h of \(\text{Ar}^+\) sputtering (energy 1 keV, current density \(\sim 5\) \(\mu\)A/cm\(^2\)), 2 h of annealing in UHV at 1050 K, and 1 h of annealing in an oxygen partial pressure of \(5 \times 10^{-6}\) mbar at 1020 K. In the following the cases with differing preparation conditions are explicitly mentioned. Surface contamination was below the level of detection of x-ray induced photoemission (XPS). Preparation cycles were repeated several times, and the resulting surfaces were checked by low-energy electron diffraction (LEED) and photoemission measurements in the ultraviolet. After successful preparation, the sample was transferred into the scanning tunneling microscope (STM) station. All STM measurements were performed with a tungsten tip, in constant current mode, and at room temperature. The shown STM images are unfiltered data apart from background correction and Fourier filtering where indicated.

![Color online](https://example.com/image.png)  
FIG. 2. (Color online) (a) 20\(\times\)20 nm\(^2\) STM image of a surface with regular structure (\(r\)) and some adsorbates, \(I=0.1\) nA and \(U_{\text{Gap}}=+1\) V. (b) Corresponding LEED pattern. (1,0)-class reflexes are labeled. \(E=47.4\) eV.

III. RESULTS AND DISCUSSION

A. Regular surface structure

After applying the standard \textit{in situ} surface preparation, STM measurements with atomic resolution yielded typical images like the one in Fig. 2(a). It shows a hexagonal array of atomic protrusions with a lattice constant of \(6.2 \pm 1.1\) Å and a corrugation amplitude of up to 1 Å. The step edge in the upper left corner of the image is aligned along the [1\(\bar{1}\)0] direction and has a height of \(4.8 \pm 1\) Å. The bright triangular features, which are monitored in Fig. 2(a) as to reside above the closed layer of atomic protrusions, can be assigned to adsorbates. Actually, upon reversing the tunneling gap voltage, these clusters appear to lie deeper than their surroundings. Such kind of tunneling voltage dependent imaging is typical for adsorbates and has been reported before for other adsorbate-substrate systems like C on Al (111).\(^14\)

The corresponding LEED pattern is displayed in Fig. 2(b). The (0,0) diffraction spot is concealed by the electron gun, the (0,1) and (1,0) spots are indicated in the image. The (2,0)-class reflexes are also visible at this electron energy. From the LEED pattern, we derive a hexagonal lattice constant of \(5.9 \pm 0.4\) Å, in good agreement with the value above found by STM. Our STM and LEED results for this type of surface structure are consistent with previous reports for the
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B. Superstructures 1 and 2

Starting from a stoichiometric magnetite surface, we performed cycles of sputtering and annealing in UHV without oxidation steps in order to systematically reduce the surface owing to the preferential sputtering of the lighter O$^{2-}$ ions. After each cycle, we carefully checked the resulting surface for indications of new atomic arrangements. Indeed, after typically about three cycles, we were able to identify reproducibly two superstructures, s1 and s2, besides the regular structure r. In Fig. 3(a), a region is shown where all three structures coexist and are clearly discernible. From the statistics on all recorded STM micrographs, we estimate that typically still about 90% of such a surface displays the regular structure while only 10% consists of the two superstructures 1 and 2. Apparently, the O deficiency after sputtering is vastly compensated by the diffusion of O from the volume to the surface during annealing. This compensation is less effective, for obvious topological reasons, at exposed locations such as steps. It is at such locations where the development of the superstructures begins, while the regular structure persists in topographically deepened regions. This situation can also be seen in Fig. 3(a).

A close-up view of the borderline region between superstructures 1 and 2 is depicted in Fig. 3(b). The borderline between s1 and s2 is made of a trench which is neither straight nor smooth. Both superstructures can be described as a quasihexagonal array of partial structures, namely, s1a, s1b, s1c and s2a, s2b, s2c, respectively [see Fig. 3(b)]. Each substructure appears distinctly separated by indentation lines. The atomic configuration could not be resolved in all detail for the various partial structures [cf. Figs. 4(a) and 4(b)], but both superstructures clearly differ at least in their partial structure c: whereas s2c appears elevated with respect to the surrounding substructures, s1c appears to be deepened [see Fig. 3(b)]. As regards the atomic arrangement, s2c is essentially congruent with the regular structure [see Figs. 4(a) and 4(b)], while no statement is possible for s1c due to the lack of atomic resolution at the bottom of the hollow.
From the overall reducing treatment of the sample surface and the fact that we could detect only the regular structure besides the superstructures 1 and 2, we can conclude that the latter should correspond to an iron enriched surface layer as compared to the regular termination. Looking at the possible bulk terminations of magnetite in Fig. 1, the natural candidate would be a \( Fe_{\text{oct}} \) termination, which corresponds to a 3/4 ML of iron. Given that s1 and s2 behave as positive and negative replicas of each other as discussed above, the formation of either s1 or s2 can simply be understood as being due to either some excess O or Fe, respectively. This gives rise in s2 to the elevated regions with regular structure or, vice versa, the hollow regions for s1. The quasi-hexagonal array of substructures in s1 and s2 with long-range order probably results from the minimization of electrostatic and strain energies. In detail, the regions or substructures which display almost no atomic corrugation we ascribe to the bulk termination at the \( Fe_{\text{oct}} \) crystal plane of \( Fe_{1-x}O \), i.e., to a closed monolayer of \( Fe_{\text{oct}} \) ions on an \( O_2 \) layer [cf. “Fe\(^{3+}\)-O-like configuration” in caption of Fig. 4(b)]. On the contrary, the substructures b, which show marked atomic corrugations, we attribute to a 3/4 ML of \( Fe_{\text{oct}} \) ions on an \( O_2 \) layer [cf. “3/4 ML, magnetite bulk terminated, 6 Å” in caption of Fig. 4(b)].

The formation of superstructures with three partial structures and a periodicity length of 50±5 Å on a reduced \( Fe_3O_4 \) (111) surface has also been reported by Condon et al.\(^\text{12}\) In that study, the superstructure is explained as a long-range ordered arrangement of \( Fe_{1-x}O \) islands on an \( Fe_3O_4 \) (111) substrate. The dimension of the \( Fe_{1-x}O \) islands is limited because of the difference of the respective lattice constants and the resulting elastic strain. Thus both other partial structures are terminated as a magnetite layer. The surface consists of a long-range ordered mosaic of different iron oxide phases (biphase ordering).\(^\text{12,16}\) Domains of both iron oxides which exhibit a well-defined lattice constant array and are exactly zoned. Indeed, the trenchlike indentations which separate the respective partial structures can be interpreted well as domain boundaries [see Fig. 3(b)]. Their low apparent height displays a topographical contrast.

The LEED pattern shows spots corresponding to magnetite as well as spots corresponding to \( Fe_{1-x}O \). Satellites surrounding the \( Fe_{1-x}O \) main reflexes stem from the long-range order of the \( Fe_{1-x}O \) lattice. The absence of satellites around the magnetite reflexes is not quite clear. A certain degree of disorder of the superstructure might be the reason for the lack of or the very low intensity of these satellites.\(^\text{12}\)

C. Superstructure 3

After further preparation cycles under reducing conditions, i.e., sputtering and annealing without oxidation steps, a third previously unreported superstructure s3 was revealed by STM [see Fig. 5(a)]. It is characterized by a distinct contrast due to a large corrugation amplitude on the scale of the superstructure periodicity length and can clearly be distinguished from the regular structure. Between adjacent terraces with superstructure 3, minimal step heights of 2.4±0.5 Å were observed, which accord very well with the distance...
between two O layers along the [111] direction of both the Fe₃O₄ and Fe₁₋ₓO bulk crystal structures. Equivalently, this height corresponds to the distance along [111] between two Fe layers in Fe₁₋ₓO, or between an Fe oct₁ and an Fe oct₂ layer in magnetite, respectively. Only steps corresponding to this minimal step height or multiples of it were observed. As is reproduced in Figs. 5a and 5b, we find coexistence of the regular structure and superstructure 3, but could not detect areas of s₁ and s₂, respectively. Other nonequivalent step heights are labeled in Fig. 5a. In particular, the step height from a terrace with regular structure down to a terrace with superstructure 3 amounts to 1.5±0.5 Å, which matches the vertical distance from an Fe tet₁ to an Fe oct₁ layer in bulk magnetite, namely, 1.8 Å. Hence, from the observed step heights, we conclude that a termination of s₃, which is equivalent to or derived from either the Fe layer in Fe₁₋ₓO or the octahedrally coordinated Fe layers in Fe₃O₄ (i.e., Fe oct₁ and Fe oct₂), is most likely.

Images of superstructure 3 with atomic resolution are presented in Figs. 6a and 6b. Here, an area of the sample was simultaneously imaged with negative and positive gap voltages, which relates to tunneling into occupied and unoccupied states, respectively. An atomic lattice constant of 3.3±0.6 Å and a superlattice periodicity of 49.3±5 Å were measured, corresponding to a 15×15 superstructure. The superstructure shows different behaviors employing negative and positive gap voltages, respectively. While the inner of the partial structures a, b, and c as well as their heights do not change by varying the gap voltage, the borderline regions between them appear different such that their geometrical shape alters dramatically. Therefore, for both signs of the gap voltage, the corrugation amplitude of the bare superstructure can be conceived as a form of topographical contrast, whereas the borderline regions seem to display electronic contrast. A difference between the lattice constants of the various partial structures can neither be confirmed nor excluded from our STM micrographs so far.

In an attempt to pinpoint the nature of the s₃ termination, a look at the LEED pattern (see Fig. 7a) of the same surface as in Figs. 5 and 6 is helpful. Symmetry and size of the
accomplished by a single sputtering and annealing cycle prepare a surface made up only of superstructure 3. This was and the superstructure s3.

position of the diffraction spots from the regular structure we interpret the LEED pattern in Fig. 7

been exposed to air for several weeks. In the corresponding LEED picture shown in Fig. 7

p shows a comparison of Fe 2

s

tive analysis of the LEED pattern in Fig.7

flexes are missing. Upon careful inspection and a quantita-

3. The charge transfer satellites are indicated.

In addition to this qualitative information, we determined the surface composition from the integral intensities of the Fe 2p and O 1s lines after a Shirley background was subtracted and taking into account correction factors for orbital asymmetry, photoionization cross sections, kinetic energy dependent inelastic mean free paths, and analyzer transmission. Table I shows the obtained Fe/O ratios for three emission angles with respect to the surface normal, i.e., three different probing depths d. For medium angles up to 66°, i.e., probing depths of 12 Å and larger, almost the ideal stoichiometries of Fe3O4 and FeO are found for the regular structure and superstructure 3, in complete agreement with our reasoning above. Only for probing depths as small as 5 Å is a sizable deviation from the ideal stoichiometries observed, which, however, remains small for superstructure 3. Therefore the film thickness of the Fe1-xO-like layer is estimated to be larger than ~19 Å.

To summarize the discussion so far, superstructure 3 can be characterized as follows: (1) From the course of the experiment and the treatment of the sample surface, one can expect that s3 corresponds to a more strongly reduced sur-

| Table I. Fe/O ratio of surfaces with regular structure and superstructure 3 calculated for three emission angles (θ is emission angle with respect to surface normal) and electron escape depths, respectively. |
|---------------------------------|-----------------|-----------------|
| Fe/O ratio (±0.1)               | Regular structure | Superstructure 3 |
| θ=81° (d~ 5 Å)                  | 0.41             | 0.83             |
| θ=66° (d~ 12 Å)                 | 0.75             | 1.03             |
| θ=51° (d~ 19 Å)                 | 0.73             | 0.97             |

We now turn to the electronic structure of the regular structure and a surface with superstructure 3. The charge transfer satellites are indicated.

3. The charge transfer satellites are indicated.

FIG. 8. (Color online) Fe 2p XPS spectra of a surface with regular structure and a surface with superstructure 3. The charge transfer satellites are indicated.

unit cell are identical for all bulk terminations of magnetite. If, as suggested above as one possibility by the observed step heights, the unreconstructed bulk terminations are exposed in s3, the symmetry of the LEED pattern should not change as compared to that of the regular structure in Fig. 2(b). However, as can be seen in Fig. 7(a) in addition to the (1,0)- and (2,0)-class reflexes, there appear additional spots surrounding every (2,0)-class reflex. We argue that these new reflexes [see arrow in Fig. 7(b)] correspond to a nonmagnetcite structure with a lattice constant of 3.24±0.19 Å, which matches nearly the value 3.04 Å for an Fe1-xO main reflex. Thus, we interpret the LEED pattern in Fig. 7(a) as being a superposition of the diffraction spots from the regular structure and the superstructure s3.

This interpretation was substantiated as we happened to experiment and the treatment of the sample surface, one can expect that s3 corresponds to a more strongly reduced sur-

FIG. 7. (a) LEED pattern of a surface with superstructure 3 and the regular structure corresponding to Fig. 5(a); E=47.3 eV and Fe3O4 main reflexes are indicated. (b) LEED pattern of a surface with superstructure 3 corresponding to Fig. 6; E=47.3 eV. The arrow points at an Fe1-xO main reflex.

In order to narrow down the possible terminations of s3 from another direction, we investigated the chemical composition and electronic structure by means of XPS. Figure 8 shows a comparison of Fe 2p core-level spectra of homogeneous surfaces with either regular structure or superstructure 3. The charge transfer (CT) satellites arising from different conduction-band screening of the Fe 2p core hole created at either the Fe2+ or Fe3+ ions are differently weighted in both spectra. The Fe2+ CT satellite is much more intense in the spectrum of superstructure 3, which clearly indicates a reduced state. Also both main lines of the spectrum of superstructure 3 are shifted to lower binding energy, reflecting the relative chemical shift between Fe2+ and Fe3+ states. This again signals the reduced character of the s3 surface.

| Table I. Fe/O ratio of surfaces with regular structure and superstructure 3 calculated for three emission angles (θ is emission angle with respect to surface normal) and electron escape depths, respectively. |
|---------------------------------|-----------------|-----------------|
| Fe/O ratio (±0.1)               | Regular structure | Superstructure 3 |
| θ=81° (d~ 5 Å)                  | 0.41             | 0.83             |
| θ=66° (d~ 12 Å)                 | 0.75             | 1.03             |
| θ=51° (d~ 19 Å)                 | 0.73             | 0.97             |
face composition than the regular structure. (2) The LEED pattern in Fig. 7(b) shows clearly that superstructure 3 is not based on a bulk termination of magnetite, but rather corresponds to a Fe_{1−x}O-like surface. On the other hand, the pattern is not what one would expect for a simple reconstruction of an Fe_{1−x}O-layer because most of the superstructure spots are missing in between the main reflexes. (3) As for the XPS Fe 2p spectra, the observed CT satellite structure is typical for Fe_{1−x}O, not for Fe_{2}O_{4}. In addition, the Fe/O ratio is approximately 1. (4) STM measurements show that the step height between equivalent terraces amounts to 2.4 Å, which is at variance with the vertical periodicity length of bulk magnetite.

While, thus, it seems clear that the chemical composition of s3 is that of Fe_{1−x}O, the structural findings need some further considerations. First, the boundaries between partial structures are not exactly defined as should be the case for a biphase ordered structure. Furthermore, the inner arrangement and the lattice constants of the partial structures do not vary significantly. Hence, s3 should not be described as an ordered arrangement of different iron oxide domains.

Next one has to understand the LEED picture. At first glance, it bears similarities to the diffraction pattern of a Moiré-like superstructure, where multiple diffraction on two superimposed rigid lattices yields additional spots which appear to decorate the main reflexes of the two lattices. In our case, these lattices could correspond to magnetite as substrate surface and a very thin Fe_{1−x}O overlayer. Alternatively, the two lattices could both relate to Fe_{1−x}O but with differing lattice constants, i.e., to a strained overlayer and an incoherent interface, which seems to be more likely since magnetite reflexes are completely absent. Such Moiré-like patterns have been observed, e.g., on epitaxially grown films of Fe_{1−x}O on Pt(111), which were notably smaller than 19 Å. However, there is yet another possibility to obtain such a LEED pattern, namely, through a vertical lattice undulation of the substrate surface as was observed, e.g., on epitaxially grown layered chalcogenides. Here, the weak van der Waals forces between the layers ease such a deformation of the topmost layer. Another example is Ge on Si(111). There the interfacial misfit is adjusted by a network of dislocations, which causes the vertical modulation. The small elastic lattice deformation surrounding every dislocation generates a small periodic vertical undulation of the surface and hence a spot splitting in the LEED pattern. In this scenario, the overlayer is thick and plastically relaxed, and a coherent or semi-coherent interface is formed. As has recently been shown, not only the formation but also the ordering of misfit dislocations can be regarded as a relaxation mechanism. In our case, this situation would correspond to a relaxed, relatively thick Fe_{1−x}O overlayer on a magnetite substrate, where strain relieving misfit dislocations are introduced at the interface. From the genesis of the superstructure 3 out of the bulk, under thermodynamic equilibrium conditions after the initial sputtering where a classical growth model certainly does not apply, we actually favor this latter mechanism. Note that similar conclusions were arrived at in another oxide, viz., Nb_{x}Ti_{1−x}O_{2}. In summary, we interpret superstructure 3 as a strained and vertically deformed overlayer of Fe_{1−x}O on an Fe_{2}O_{4} selvedge. This overlayer is relatively thick (>19 Å) and thus corresponds to a more reduced state than the structure previously reported by Condon et al. It is not clear if there is a well-defined Fe_{1−x}O-Fe_{2}O_{4} interface. Hence it remains questionable if a growth model can be applied.

D. Microscopic origin of superstructure 3

A superstructure similar to superstructure 3 but for an oxygen-rich magnetite surface (O/Fe ratio=1.45 as determined by Auger electron spectroscopy) was observed by Berdunov et al. It has a periodicity of 42±3 Å and also consists of three partial structures. The superstructure corrugation was interpreted as an electronic rather than a structural effect because of different tunneling conductances of the partial structures. It was claimed that an electron lattice instability giving rise to, e.g., localized polarons or a charge density wave (CDW) triggers the formation of the superstructure. One could argue that similar mechanisms are at work here. However, concerning the latter, there is no substantiated theoretical or experimental hint for a CDW bulk phase in magnetite—e.g., because of hidden one dimensionality—which could induce a surface CDW due to a kind of proximity effect, nor is there any reason to expect a genuine surface Peierls phase due to the fact that the specific surface electronic structure would favor Fermi surface nesting conditions in contrast to the bulk. Actually, there exist only very few and atomically “clean” metal or metaloxide systems, which were discussed under the notion of surface Peierls phases. Jahn-Teller (i.e., small) polaron formation together with short-range Coulomb repulsion have recently been identified to be the key ingredients in understanding the electronic structure and, in particular, the Verwey phase transition in bulk magnetite. Both can be considered in the first place as locally, i.e., with respect to a tetrahedron of the pyrochlore lattice, lowering the energy balance. As such, both will, in an analogous way, certainly play a role also at the surface. However, this local energy gain following electron-lattice coupling cannot explain the development of long-range superstructures with huge periodicity length. Here, the energy balance is dominated by strain vs. electrostatic energy as in growth mode models, which is achieved not locally but over larger surface regions as reflected in the domain type areas in s3 with a diameter of about 45 Å.

Such an approach to consider minimum energy surface configurations is pursued theoretically by density functional slab layer calculations or—as an extension of these—ab initio thermodynamics. While the former approach has been successfully applied to semiconductor surfaces like Si or GaN, the latter is especially suited for oxide materials since it additionally allows taking into account the chemical conditions during surface preparation through the thermodynamic coupling of the surface slabs to an O gas reservoir. Thus the relative stability for various stoichiometric and nonstoichiometric surface terminations can be determined. Up to now, there have been only a few studies which applied ab initio thermodynamics to binary oxides, in particular, to various iron oxide surfaces. The studies on Fe_{2}O_{4} (001)
(Ref. 25) and Fe$_3$O$_4$ (111) (Ref. 6) interestingly both identify, among the investigated surface configurations, an octahedral iron-terminated surface as the most stable one in a range corresponding to our experimental reducing preparation conditions. In case of Fe$_3$O$_4$ (111), it is actually the unreconstructed bulk termination. This is in line with our experimental findings for superstructures s1 and s2, for which we also identify a bulk derived octahedral iron termination. However, the current limitations of ab initio thermodynamics is strikingly demonstrated by the formation of complex superstructures which cannot be reconciled by theory so far. Moreover, phenomena where the surface region switches beyond relaxation and reconstruction to another iron oxide phase as observed for superstructure 3 are beyond the scope of such calculations. In order to understand the complexity of magnetite surfaces—and oxide interfaces in general—against the background of tailoring chemical, electronic, and magnetic properties of heterostructured materials for prospective device applications, theoretical concepts taking into account the kinematics of surface formation under realistic conditions have to be developed.

IV. SUMMARY

The existence of several structures on the Fe$_3$O$_4$ (111) surface has been demonstrated for different reducing preparation conditions. The stoichiometric surface corresponds to the regular Fe$_{net}$ termination. Slightly reduced surfaces can be interpreted as biphasic ordered structures. A superstructure on an even more reduced surface has been identified as a complete overlayer of Fe$_{1-x}$O formed on top of bulk magnetite. Thus our results show the wealth of structures which exist for the Fe$_3$O$_4$ (111) surface and their subtle dependency on the preparation conditions. These findings have to be considered in the search for potential applications exploiting tailor-made physical properties of oxide materials in general, e.g., of Fe$_3$O$_4$ (111) layers as spin aligner in prospective spintronic devices.

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