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Ferryl (Fe═O) Termination of the Hematite α-Fe_2O_3(0001) Surface

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Using scanning tunneling microscopy and infrared reflection absorption spectroscopy we have observed that the α-Fe_2O_3(0001) surface exhibits ferryl (Fe═O) groups, which may coexist with domains of the Fe-terminated surface. We therefore fully support *ab initio* calculations recently reported in the literature [W. Bergmeyer, H. Schweiger, and E. Wimmer, Phys. Rev. B **69**, 195409 (2004)]. The close similarity to the results on the (0001) surfaces of Cr_2O_3 and V_2O_3 strongly suggests that the *M*═O termination under certain oxygen pressure conditions is the most stable for the close-packed surfaces of transition metal oxides with the corundum structure.

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Surface structures of transition metal oxides often deviate from those expected from the cleavage of the oxide bulk. In particular, it has been shown that oxides with corundum structure (such as Cr_2O_3, V_2O_3) may be terminated by metal-oxygen double bond species (Cr═O, V═O) absent in the bulk [1–3]. From simple electrostatic considerations, the stable corundum surface is expected to be the metal-terminated stoichiometric surface *M*-O_3-*M*-*M*-*R* (the subscript denotes the number of atoms in a layer in the unit cell; see Fig. 1), which has the same number of cations above and below the oxygen anion layer. It has been theoretically predicted that the surface structure of α-Fe_2O_3(0001), which is isostructural to chromia and vanadia, should depend on the ambient oxygen pressure such that, at high pressures, an oxygen-terminated surface becomes lower in energy than the iron-terminated layer that is stable at low O_2 pressures [4]. Both surfaces are unreconstructed and stabilized by strong relaxations. This hypothesis has been substantiated by scanning tunneling microscopy (STM) studies of Fe_2O_3(0001) films prepared at different oxygen pressures [5]. Two different surfaces were observed, which were assigned to the O_3 and Fe terminations according to the theoretical predictions. However, based on dynamical LEED studies of the films, Ketteler *et al.* [6] suggested that the surface, prepared at 10^{-5} mbar O_2, may be hydroxyl terminated due to reactions with traces of water. On the other hand, Chambers and Yi, employing x-ray photoelectron diffraction on the films prepared by oxygen plasma assisted epitaxy, conclude that the surface is Fe terminated despite the highly oxidizing conditions used [7]. Recently, Bergmeyer *et al.* [8] and Rohrbach *et al.* [9] theoretically predicted relative stability of ferryl (Fe═O) groups on the hematite surface, which is rather surprising. Indeed, while Cr═O and V═O double bonds are well known species in chemistry of Cr and V compounds, Fe═O species are very rare and mainly considered as an active center in heme containing enzymes.

In this Letter, using infrared reflection absorption spectroscopy (IRAS), we present the first experimental evidence that the ferryl groups indeed exist on the α-Fe_2O_3(0001) surface. We use density functional theory (DFT) to calculate the vibrational properties of the ferryl groups.

The bulk structure of α-Fe_2O_3(0001) is schematically shown in Fig. 1. Along the axis normal to the surface the stacking sequence of hexagonal iron and oxygen layers can

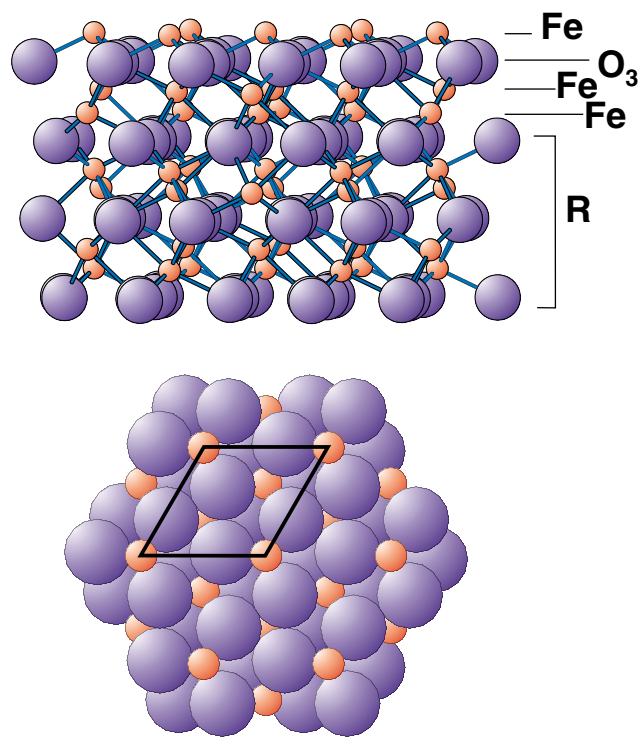

FIG. 1 (color online). Perspective side and top views of α-Fe_2O_3(0001). The Fe-terminated surface is shown, with the unit cell indicated.

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be described as $\cdots$ Fe-O_3-Fe-Fe-O_3-Fe $\cdots$. The Fe layer forms a $(\sqrt{3}x\sqrt{3})R30°$ structure with respect to the close-packed oxygen layer, resulting in an Fe-Fe distance of 5.03 Å, which is the lattice constant of the surface unit cell. The distance between two identical planes is 2.29 Å.

To study the hematite surfaces, we prepared well ordered $Fe_2O_3(0001)$ films on a Pt(111) substrate in 10^{-3}–1 mbar of O_2 at ~1050 K [5]. The films of 5–7 nm in thickness exhibited sharp low energy electron diffraction patterns. In one chamber, the samples were studied with STM at room temperature and temperature programmed desorption (TPD) of CO. In a different chamber, we employed IRAS and TPD. In both chambers, we used the same preparation conditions and obtained essentially identical CO TPD spectra, which allowed us to combine results from the two chambers.

Theoretical calculations were performed on bulk and slab geometries in the conventional hexagonal unit cell representation using spin-polarized all-electron first principles DFT and DNP (double numeric with polarization) basis sets as implemented in the $Dmol^3$ program [10]. The generalized gradient approximation [11] was used to solve the Kohn-Sham equations. k-point sampling was performed on a 5×5 mesh and checked with a 12×12 mesh. The lowest energy structure was found to be antiferromagnetic within iron double layers. Symmetric slabs were 18 atomic layers thick and separated by 10 Å of vacuum.

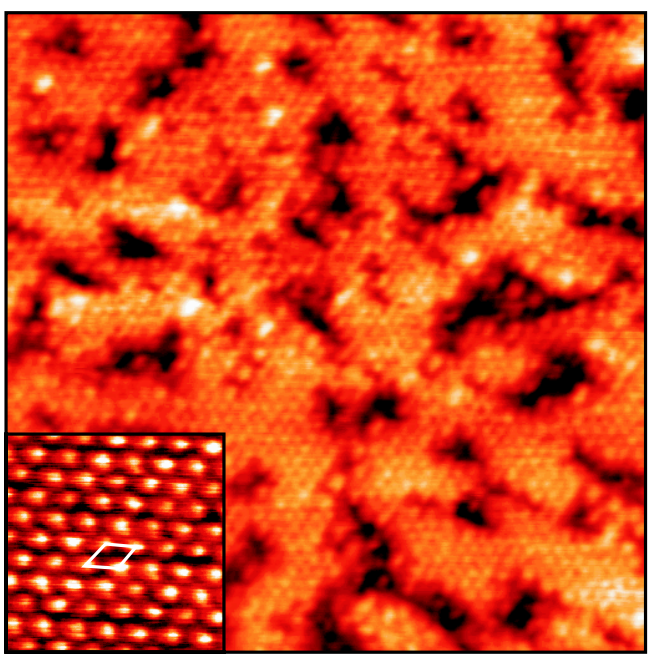

FIG. 2 (color online). High resolution STM image of the $Fe_2O_3(0001)$ film prepared in 10^{-2} mbar of O_2 at 1020 K (size 30×30 nm^2, $V_t = 1.4$ V, $I = 1$ nA). The lattice of protrusions with a ~5 Å periodicity is clearly seen in the inset (size 3×3 nm^2). The unit cell is indicated.

Large scale STM images of the $Fe_2O_3(0001)$ films revealed wide flat terraces separated by monatomic steps ~2.3 Å in height or multiples thereof. Atomic-resolution STM images of the films revealed a ~5 Å periodicity, as shown in Fig. 2. However, the terraces exhibited a heterogeneous surface with a random placement of small depressed areas. The depth of these areas is 1–1.5 Å (depending on the tunneling conditions), i.e., significantly smaller than the 2.3 Å for the monatomic step, and should therefore be assigned to a domain, exhibiting different termination.

Identically prepared samples were studied by IRAS, in which we measure relative intensities referenced to a baseline from a clean substrate or, in the case of adsorption studies, from the sample measured right before gas exposure.

Curve (1) in Fig. 3(a) shows the IRAS spectrum obtained for the $Fe_2O_3(0001)$ surface, prepared in 5×10^{-2} mbar O_2 at 1040 K, and referenced to the Pt(111) substrate. The only feature observed in survey spectra is a peak at 989 cm^{-1}. A difference spectrum (2) comparing two sur-

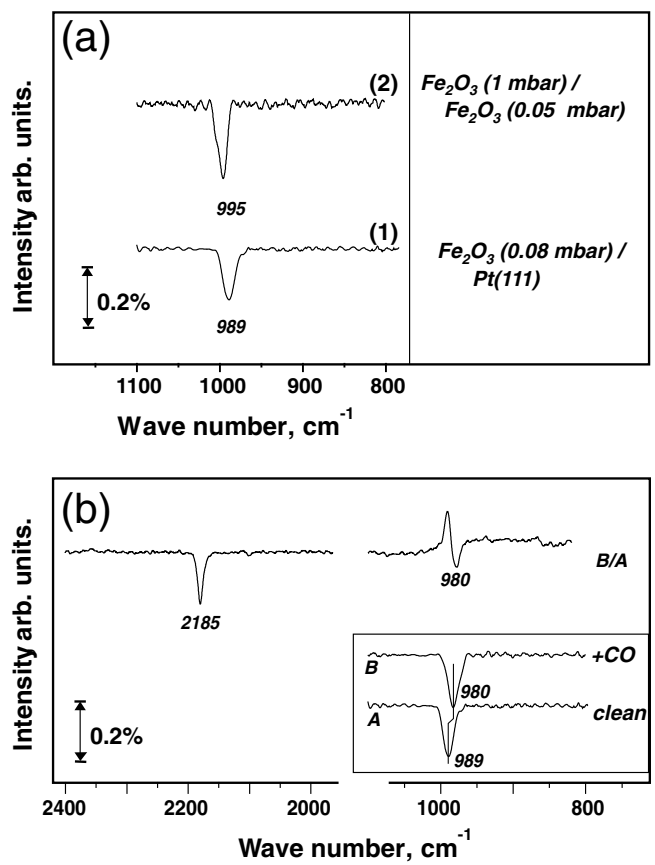

FIG. 3. (a) IRAS spectra of the $Fe_2O_3(0001)$ films. (b) CO IRAS spectrum of the Fe_2O_3 sample (1) shown in (a) after exposing to 1.5 L of CO at 90 K. The unusual peak shape at ~980 cm^{-1} results from a shift of the oxide absorption band induced by CO adsorption, as shown in the inset.

faces prepared at different O_2 pressures (0.01 and 1 mbar) clearly shows that the IR absorption in this region becomes stronger with increasing oxygen pressure.

The absorption bands at around 1000 cm^{-1} are characteristic for the stretching vibrations of the metal-oxygen double bond observed in V_2O_5, H-Nb_2O_5, and MoO_3 [12], where M═O species are present in the bulk. However, it has recently been shown that Cr_2O_3(0001) and V_2O_3(0001) films may also expose chromyl (Cr═O) and vanadyl (V═O) groups on the surface, thus resulting in IRAS signals at 1015 and 1040 cm^{-1}, respectively [1–3]. In particular, the presence of vanadyl species on the V_2O_3 films has been additionally proven by angular resolved photoelectron spectroscopy [3] and supported by theoretical calculations [13].

Our DFT calculations on the ferryl-terminated surface found a stretching frequency of 981 cm^{-1}, in excellent agreement with the observed frequency and providing strong support for the Fe═O assignment. The calculations show that the ferryl oxygen is 1.58 Å directly on top of the iron cations, which is consistent with the atomically resolved STM images, showing that the protrusions in domains with different terminations are in registry but of different corrugation amplitudes (for example, see Fig. 3 in [5]). Indeed, these protrusions are attributed to the Fe cations as the states near the Fermi level, probed by STM, are determined by Fe 3d orbitals [4]. Since ferryl is formed by placing oxygen on top of Fe, both surfaces must be in registry. The calculated relaxation of the ferryl iron from the bulk position is $\sim -20\%$, which is considerably less than the $\sim -65\%$ of the clean Fe-O_3-Fe_2-R surface. Hence the height difference between the ferryl oxygen atom and the relaxed surface Fe cation on the clean surface is 1.96 Å, i.e., larger than observed by STM (1–1.5 Å). However, oxygen must screen the electron density of Fe, thus reducing the apparent height difference and also explaining the lower atomic corrugation over the Fe═O surface [5].

We have further studied the Fe_2O_3(0001) surface using adsorption of CO as a probe molecule. The CO TPD spectra for all films studied showed only a single desorption peak at ~130 K, indicating that CO adsorbs on the Fe_2O_3(0001) surface more weakly than on the Fe-terminated Fe_3O_4(111) films ($T_{des} \sim 180$ K [14]). CO IRAS spectra show signals in two distinct regions: the peak at 2185 cm^{-1} and the signal at ~980 cm^{-1} [see Fig. 3(b)]. The peak at 2185 cm^{-1} can be assigned to the stretching vibration of CO adsorbed on the Fe^{3+} ions [12,14–16]. The unusual shape of the signal at 980 cm^{-1} results from a CO induced shift of the Fe═O vibration frequency. This is illustrated in the inset in Fig. 3(b): the signal at 989 cm^{-1} on the clean film is shifted by 9 cm^{-1} to lower wave numbers upon CO adsorption. Interestingly, such a phenomenon is essentially identical to that observed for vanadia particles deposited on alumina and silica films [17]. It seems likely that it involves direct interactions between CO and Fe═O species at the border of two domains with different terminations.

CO adsorption experiments also showed that the hematite films were not completely covered by the ferryl groups, which is in line with the STM studies showing the heterogeneity of the hematite film surface. When the intensities of the CO signal at 2185 cm^{-1} and of the Fe═O signal at 989 cm^{-1} (on the clean film) were compared to those observed for the metal and M═O terminated surfaces of Cr_2O_3 and V_2O_3 films previously studied [1,3], then the Fe═O coverage could be roughly estimated to be around 0.4 ML (referring to the Fe-terminated surface, depicted in Fig. 1, as 1 monolayer).

In contrast to vanadium and chromium oxides, where the existence of M═O species are well documented in the literature for powdered samples using conventional Fourier transform infrared (FTIR) spectroscopy, results for iron oxides are very limited [12,15]. In order to compare the results for the well ordered films and polycrystalline samples, we have performed IR studies on Fe_2O_3 powders. Figure 4 shows the 800–1200 cm^{-1} region of the spectra for the sample prepared at 973 K in 40 mbar of O_2 and another at 1023 K in 5×10^{-2} mbar of O_2, i.e., under the same conditions as the Fe_2O_3(0001) films studied by IRAS. Both samples showed only a hematite phase in the x-ray diffraction patterns and a typical needlelike morphol-

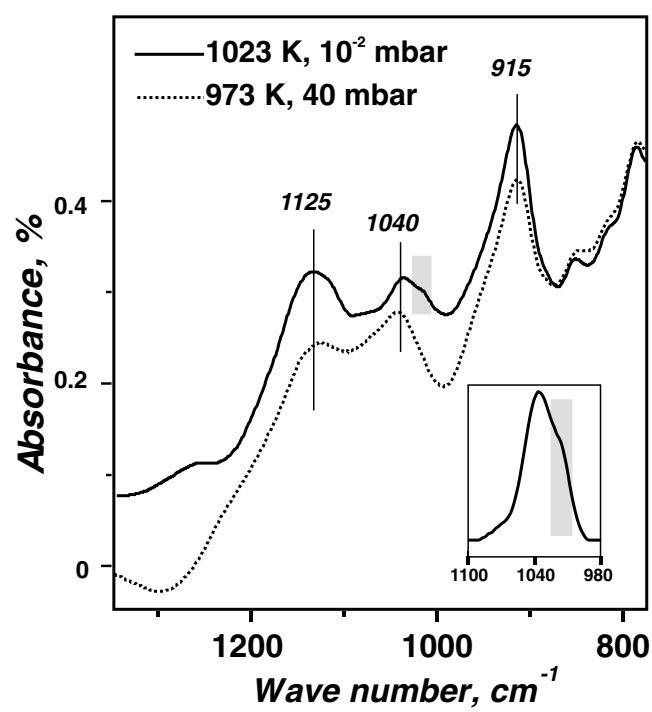

FIG. 4. IR spectra of the polycrystalline Fe_2O_3 samples prepared at 973 K in 40 mbar of O_2 (dashed line) and at 1023 K in 5×10^{-2} mbar of O_2 (solid line). The Fe═O region is expanded in the inset.

ogy of the crystallites as revealed by electron microscopy [16,18].

The absorption bands at 915, 1040, and 1125 cm^{-1} can be assigned to multiple phonon excitations [19,20]. (The fact that these bands are not observed in the IRAS spectra of the films is due to the small thickness of the films and the large contribution of the bulk absorption in IR spectra of powders in a transmission mode.) Comparing the two spectra shown in Fig. 4, one can see the presence of the prominent shoulder at $\sim$1015 cm^{-1} for the samples prepared under the same conditions as the thin films. We have assigned this feature to the ferryl species. The $\sim$25 cm^{-1} difference between the frequencies observed by IRAS for the film and by FTIR for the powder is not surprising. It has been shown for α-Cr_2O_3 powders that the Cr═O stretching frequency depends on "coordinative and ligand heterogeneity" of Cr ions and varies in the range 990–1040 cm^{-1} [21], whereas its value for the chromia films is 1005 cm^{-1} [1]. In addition, the difference between thin films and powdered systems can be attributed to the interaction with bulk phonons in powders as well as with surface species. (Note that the FTIR studies on powder are not performed under UHV conditions.) Since the surface of the hematite crystallites is predominantly the prismatic (1–10) planes and not the basal (0001) plane [15], the intensity of this feature at 1015 cm^{-1} is relatively small. This shoulder appears to be absent for the sample treated at high oxygen pressure, indicating that the ferryl species is less stable under these conditions.

Using the DFT-based *ab initio* thermodynamics methodology [22], we have calculated the surface free energies as a function of oxygen pressure. Our calculations show that the Fe═O surface becomes the most stable above an oxygen chemical potential of -1.4 eV, which corresponds to a $p(O_2)$ of 1 mbar at 1040 K and 10^{-2} mbar at 870 K, i.e., in quantitative agreement with our experiments.

The chemistry of the M═O species on the oxide surface is the subject of the on-going investigations in different groups. Our own results show that vanadyl and chromyl species present on the $M_2O_3(0001)$ surfaces are essentially inert in adsorption of many molecules such as CO, CO_2, and H_2 [1,23]. However, this is not obvious for the ferryl species. It is well documented that ferryl is a key species or intermediate in the heme containing enzymes, which efficiently oxygenate and hydroxylate saturated hydrocarbons by molecular oxygen [24]. Therefore, one can expect that ferryl species on the oxide surface may be active, for example, in selective oxidation and dehydrogenation reactions.

In summary, our experimental and theoretical results provide strong evidence that the $Fe_2O_3(0001)$ surface can form ferryl (Fe═O) groups, which coexist with domains of the Fe-terminated surface. The close similarity to the results on the (0001) surfaces of Cr_2O_3 and V_2O_3 strongly suggests that the M═O termination at certain oxygen pressure is the most stable for the surfaces of transition metal oxides with corundum structure.

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