Surface Science 671 (2018) 11–16

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Ab initio simulation of structure and surface energy of low-index surfaces of stoichiometric α-Fe_2O_3

Thomas Stirner[a,*], David Scholz[a], Jizhong Sun[b]

[a] Department of Applied Natural Sciences, University of Applied Sciences Deggendorf, Dieter-Görlitz-Platz-1, D-94469 Deggendorf, Germany
[b] Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Ministry of Education), School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian 116024, China

ARTICLE INFO

Keywords:
Hartree–Fock simulation
Surface relaxation
Surface energy
Wulff–Gibbs construction
Hematite

ABSTRACT

The structure and surface energy of a series of low-index surfaces of stoichiometric α-Fe_2O_3 (hematite) are investigated using the periodic Hartree–Fock approach with an *a posteriori* correction of the correlation energy. The simulations show that, amongst the modeled facets, (01$\bar{1}$2) and (0001) are the most stable surfaces of hematite, which is consistent with the fact that the latter are the dominant growth faces exposed on natural α-Fe_2O_3. The Fe-terminated (0001) surface is shown to exhibit a large relaxation of the surface atoms. It is argued that this arises mainly due to the fact that the surface cations are located opposite empty cation sites in the filled-filled-unfilled cation sequence along the *c*-axis. In contrast, the (01$\bar{1}$2) plane cuts the crystal through a plane of empty cation sites, thus giving rise to relatively small relaxations and surface energies. The small relaxations and concomitant exposure of five-coordinate cation sites may be important for the catalytic activity of hematite. The simulations also show that the relative stability of the investigated surfaces changes after a full lattice relaxation with the (0001) and (11$\bar{2}$6) facets relaxing disproportionately large. Wherever possible, the simulations are compared with previous simulation data and experimental results. A Wulff–Gibbs construction is also presented.

1. Introduction

Hematite (α-Fe_2O_3) is one of the thermodynamically most stable and most abundant oxides of iron in nature under ambient conditions [1]. The crystal structure of hematite is that of corundum with space group R$\bar{3}$C. It is occupied by two formula units in the primitive rhombohedral unit cell and six formula units in the hexagonal unit cell [2]. The Fe^{3+} cations occupy two-thirds of the available octahedral sites in an approximately hexagonally close-packed O^{2-} anion sublattice, leading to a filled-filled-unfilled sequence of the cation sites along the *c*-axis. There are unpaired electrons in the 3*d*-subshell of hematite. A high-spin electron configuration was demonstrated experimentally [3]. Below the Néel temperature of 960 K, hematite is antiferromagnetic. Between the Néel and the Morin temperature of 260 K, hematite shows a weak ferromagnetism due to a slight canting of the magnetic moments [4].

There is currently significant interest in hematite both from a scientific and technological viewpoint. Hematite was investigated for applications as chemical or magnetic sensor [5,6], for spintronics [7], as anode material for Lithium-ion batteries [8], for the photoelectrochemical splitting of water [9–11] and as a catalyst [12,13]. Due to the strong correlations amongst its localized 3*d* electrons, it places stringent requirements on the employed theoretical methods. Density-functional theory with a Hubbard-type on-site Coulomb repulsion (the DFT + *U* method) has been used to study hematite [14–16]. Recently, Huang et al. [17] extended this approach with site-specific U^d values and a Coulomb correction U^p to describe better the hybridization between the Fe d and O p orbitals. Liao and Carter [18] employed a many-body Green's function method with a screened Coulomb interaction W, known as the GW approximation, to investigate low-lying excited electronic states in hematite. Alvarez-Ramírez et al. [19] used four different DFT approximation levels, namely the non-selfconsistent Harris functional, the local spin-density approximation (LDA), the generalized gradient approximation and hybrid functionals, to study the surface structural relaxation of (0001) hematite. Pozun and Henkelman [20] used hybrid DFT with 12% exact exchange at short range to reproduce the experimental band gap and other material properties of hematite. Wilson and Russo [21] carried out a hybrid density functional theory study of the high-pressure polymorphs of hematite. Very recently, Meng et al. [22] used three density functional approximations, namely PBE, PBE + *U* and HSE, to investigate the structural, electronic, magnetic and thermodynamic properties of bulk α-FeOOH, α-Fe_2O_3, Fe_3O_4 and FeO. These authors found that the Heyd–Scuseria–Ernzerhof screened hybrid functional (HSE) containing 15% "screened" Hartree–Fock exchange can provide reliable values of lattice constants, Fe magnetic moments, band gaps and formation

---

[*] Corresponding author.
E-mail address: thomas.stirner@th-deg.de (T. Stirner).

https://doi.org/10.1016/j.susc.2018.01.010
Received 23 October 2017; Received in revised form 18 January 2018; Accepted 19 January 2018

energies of all four iron oxides. The hydrated hematite surface has also been studied theoretically and experimentally [23–35] and strong evidence for the presence of multiple coordination environments for the surface hydroxyl functional groups was found. In a recent work [36] we demonstrated that also the Hartree–Fock (HF) method with an *a posteriori* calculation of the correlation energy is a useful tool to investigate the structural, electronic and magnetic properties of hematite. The present work aims at extending these HF studies by calculating the surface structure and energy of a whole range of stoichiometric hematite surfaces with low Miller–Bravais indices. The relative stability of the investigated surfaces is then compared with the results of other theoretical approaches.

2. Computational details

All of the present calculations were performed with the computer code CRYSTAL14 [37], which is an *ab initio* LCAO (linear combination of atomic orbitals) Hartree–Fock program for the treatment of periodic systems. The surface is described by a slab model with 2D periodicity and the unrestricted open-shell Hamiltonian is used for Fe_2O_3 [2,38]. Since there are unpaired 3*d* electrons in isolated Fe^{3+} ions, the use of the unrestricted treatment of the spin-dependent part of the wavefunction in the open-shell systems is necessary to obtain spin-polarized eigenfunctions of the Fock Hamiltonian [39]. α-Fe_2O_3 (hematite) has the corundum-type structure. The spin sequence on the Fe atoms along the three-fold symmetry axis (i.e. Fe-3O-Fe-Fe-3O-Fe) can exhibit four different orders, corresponding to one ferromagnetic (++++) and three antiferromagnetic (+−−+, ++−− and +−+−) configurations. Although the first antiferromagnetic phase (+−−+) is the stable ground-state structure, the geometries of the latter and the ferromagnetic bulk phase are virtually identical [2]. We therefore consider here the computationally less demanding ferromagnetic structure with four spin-up symmetry related iron atoms in the primitive cell (space group $R\bar{3}C$). The all-electron level basis sets and structural parameters were taken from Ref. [2]. The surfaces we study here are the $\{0001\}$, $\{11\bar{2}0\}$, $\{10\bar{1}0\}$, $\{10\bar{1}2\}$, $\{01\bar{1}2\}$, $\{10\bar{1}1\}$ and $\{11\bar{2}6\}$ families. The repeat units (number of layers in the slab) are selected as Fe-3O-Fe… for $\{0001\}$ (21 layers), O-2O-4Fe-2O-O… for $\{11\bar{2}0\}$ (30 layers), 2O-4Fe2O-2O… for $\{10\bar{1}0\}$ (30 layers), 2Fe-2O-2O-2O-2Fe… for $\{10\bar{1}2\}$ (35 layers), 2O-2Fe-2O-2Fe-2O… for $\{01\bar{1}2\}$ (25 layers), O-Fe-O-Fe-O… for $\{10\bar{1}1\}$ (40 layers) and O-2Fe-2O-2O-2Fe-O… for $\{11\bar{2}6\}$ (36 layers), with surface terminations giving rise to a minimal dipole moment [40], although different surface terminations may occur [33,41]. These numbers of layers were found to be sufficient for a convergence of the final results. In the course of the geometry optimization, we do not place any constraints on the atoms except for the conservation of the original crystal symmetry in the two dimensions parallel to the surface. The correlation and exchange energy was estimated *a posteriori* via the Hartree–Fock density, i.e. only the initial HF simulation is variational and the *a posteriori* calculation is a single point simulation. Various hybrid functionals were employed in the *a posteriori* calculation, namely B3LYP, B3PW, PBE0 and M06. The fully relaxed positions of all atoms in the simulation cell for all considered surfaces are provided in Section S1 of the Supplementary Material. We have also variationally relaxed the (0001) slab with the B3LYP hybrid functional and have found the differences in the obtained atomic positions compared to the HF results almost negligible. The positions of all atoms in the simulation cell for the B3LYP-relaxed slab are provided in Section S2 of the Supplementary Material.

In the CRYSTAL code the level of numerical approximation in evaluating the Coulomb and exchange contributions to the Hartree–Fock matrix is controlled by five tolerances [37]. The values used in the present calculations are (7 7 7 7 14). The shrinking factors, which determine the number of sampling points in the irreducible Brillouin zone (IBZ), were chosen as (6 6 6) and (6 6) for the bulk and slab, respectively. As a result, there are 32 *k*-points in the bulk IBZ and 8 *k*-points in the slab IBZ. Other parameters for controlling the geometry optimization process are the same as in Ref. [36]. Checks with varying tolerances and numbers of *k*-points showed the final results of the calculations to be robust. The surface energy at zero temperature is computed by $E_S = (E(n) - n\, E_{bulk})/(2A)$ following the description of Vitos [42], where A is the area of the primitive surface unit cell, $E(n)$ is the energy of a n-unit layer slab, and E_{bulk} is the energy of a unit layer of the bulk. We have checked this value of the surface energy against calculations using the methods described by Boettger [43] and Fiorentini and Methfessel [44], and have found agreement between these methods to within approximately 3%.

3. Results and discussion

3.1. Surface relaxation

For the (0001) hematite slab we have recently shown [36] that the calculated changes in the top four interplanar spacings are −56%, + 3%, −47% and + 20% (−58%, + 6%, −45% and + 18% using the B3LYP hybrid functional) in good agreement with DFT + *U* calculations [15] and in reasonable agreement with recent low-energy electron diffraction (LEED) experiments [45]. Each Fe atom at the (0001) surface is separated by a distance of 1.945 Å from its three nearest O neighbors before relaxation. After relaxation the Fe–O distance decreases to 1.791 Å (i.e. a change of −7.9%), the nearest O–O distance increases from 2.665 to 2.833 Å and the side length of the equilateral O triangle remains with 3.035 Å virtually unchanged. The computed values for fully relaxed bulk hematite are 1.960 Å for the nearest Fe–O distance, 2.648 Å for the nearest O–O distance and 3.056 Å for the side length of the equilateral O triangle. Using an analysis of coaxial impact-collision ion scattering spectroscopy (CAICISS) data, Osaka et al. [46] obtained a shortening of the surface Fe–O bond by 6.5%, and side lengths of the equilateral O triangles of 3.04 Å for bulk and 3.13 Å for the relaxed Fe-layer termination of (0001) hematite. The corresponding three O atoms were found to rotate by 4° clockwise with the nearest first-layer Fe atom as a rotational axis [46]. In our present simulations we find a rotation by 2.8° anticlockwise. These authors also obtained interlayer separations of 0.19, 1.06, 0.27 and 0.94 Å for the first four interplanar spacings [46], which compares reasonably well with our present results of 0.37, 0.87, 0.32 and 1.01 Å.

The $(11\bar{2}0)$ surface was represented by an oblique Bravais lattice in the plane with lattice constants $a = 5.427$ Å and $b = 7.403$ Å at an angle $\gamma = 95.85°$ before relaxation. After relaxation, these values are $a = 5.437$ Å, $b = 7.328$ Å and $\gamma = 95.71°$. The structure of the slab with the $(11\bar{2}0)$ hematite surface is shown in Fig. 1 before and after relaxation. As can be seen from this figure, the layers containing four Fe atoms split upon relaxation into two layers containing two Fe atoms each. However, the resulting interlayer spacings (0.062 and 0.079 Å) are significantly smaller than the remaining distances. Marked changes in the layer structure can be observed up to and including the third and fourth Fe_2 layer. The magnitude of the relative relaxations of the various layers is with around 22% quite similar, with the exception of one of the central O_2–O distances which exhibits an expansion by 39%. Furthermore, the O atoms on either side of the Fe layers approach the Fe atoms noticeably, whilst the O atoms themselves tend to increase their separation in general. The latter can be explained predominantly in terms of simple electrostatic interlayer interactions. The bottom two interlayer separations in Fig. 1 display essentially bulk behavior.

The $(10\bar{1}0)$ surface was modeled by a right-angled Bravais lattice in the plane with lattice constants $a = 5.035$ Å and $b = 13.747$ Å before relaxation. After relaxation, these values are $a = 5.0355$ Å and $b = 13.776$ Å. The structure of the slab with the $(10\bar{1}0)$ hematite surface is shown in Fig. 2 before and after relaxation. As can be seen from this figure, the second layer which has initially six atoms in the primitive cell splits into three layers, each containing two atoms. The two oxygen atoms move outwards and the four iron atoms move inwards. Two of the four iron atoms even penetrate the original third layer and form the