

Structure and magnetic properties of the $\text{Fe}_3\text{O}_4(001)$ surface: *Ab initio* studies

C. Cheng*

Department of Physics, National Cheng Kung University, Tainan, Taiwan, Republic of China

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First-principles calculations are employed to study four frequently proposed surface models for the $\text{Fe}_3\text{O}_4(001)$ surface, i.e., the *A*-terminated surface (*A* model), the *A*-terminated surface with Fe vacancy (*A*-vac model), the *B*-terminated surface (*B* model), and the *B*-terminated surface with O vacancy (*B*-vac model). However, calculations have revealed that the outmost surface Fe atoms of the four surface models are all from the *B*-type layers, i.e., the *A*-site Fe atoms which were originally situated at the surface, according to the ideal bulk-terminated positions for the *A* and *A*-vac models moved underneath the next *B*-type layer following relaxation processes. Magnetic degradation of the four surface models is demonstrated to be mainly due to atomic relaxations. The half-metallic property remains in the *B* and *B*-vac models but destroyed in the *A* and *A*-vac models. The relative stability of the four surface models is also discussed.

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Thin films of ferrites have technological importance as catalysts, anticorrosives, and magnetic devices. In particular, magnetite, as a half-metallic material, is an attractive candidate for applications in spin electronics and magneto recording. In applications of magnetite in thin magnetic films the morphology of the layers as well as the structure and composition of the surface are crucial factors for the functionality. In this respect, knowledge of the surface structure on an atomic scale is important for understanding the electromagnetic behavior of Fe_3O_4 thin films. Despite this fact there is still a lot of controversy on the termination and the structure of the (001) surface of Fe_3O_4 .¹⁻³ We have used *ab initio* methods to study the (001) surface properties of Fe_3O_4 . Calculations show interesting results of atomic relaxations near surfaces which are beyond the conventional conjectures and also provide information on how the degradation of magnetic properties on the surface arises.

Bulk Fe_3O_4 has a cubic inverse-spinel structure at room temperature where the O^{2-} anions form a fcc lattice, one-third of the Fe ions (Fe^{3+}) occupy the tetrahedral interstices (*A* sites), and the other two-thirds of the Fe ions (half Fe^{3+} and half Fe^{2+}) are located in the octahedral interstices (*B* sites). Seen from the (001) face of the crystal, the bulk unit cell can be described by four pairs of alternating atomic sublayers, which are shifted in the plane of the layer with respect to each other. Within a pair, one sublayer is composed of the *A*-site Fe^{3+} cations and the other sublayer is composed of the *B*-site Fe^{3+} , Fe^{2+} cations, and O^{2-} anions. Up to date, a significant number of attempts has been undertaken to understand the structural changes taking place at the $\text{Fe}_3\text{O}_4(001)$ surface. However, the experimental results until now have not led to a consistent determination of the atomic arrangement of the surface layer.

In the present study, we performed *ab initio* calculations to investigate the structural and magnetic properties of four frequently proposed $\text{Fe}_3\text{O}_4(001)$ surface models, i.e., the *A*-terminated surface (*A* model), the *B*-terminated surface (*B* model), and the *A*-vac and *B*-vac models. The *A*-vac model is the *A* model with an ordered array of tetrahedral Fe vacancies (half monolayer of Fe) and the *B*-vac model is the *B* model with one O vacancy per ($\sqrt{2} \times \sqrt{2}$) surface.

The total energy of systems is determined in the frame-

work of spin-polarized density functional theory.⁴ The proposed generalized gradient approximation by Perdew and Wang⁵ is used for the nonlocal correction to a purely local treatment of the exchange-correlation potential and energy. The single-particle Kohn-Sham equations⁶ are solved using the plane-wave-based Vienna *ab initio* simulation program (VASP) developed at the Institut für Material Physik of the Universität Wien.⁷ The interactions between the ions and valence electrons are described by the projector augmented-wave method⁸ in the implementation of Kresse and Joubert.⁹ The numbers of treated valence electrons are 8 and 6 for Fe and O atoms, respectively. The energy cutoff for the plane-wave basis is 400 eV in all calculations. The Monkhorst-Pack¹⁰ method of sampling *k* points is used for the Brillouin-zone integration.

The calculated lattice constants (a_0) for the cubic bulk Fe_3O_4 is 8.308 Å and the *u* parameter is 0.0044; they compare well with the experimental values¹¹ of 8.394 Å and 0.0048. Here the *k*-point set used corresponds to the Monkhorst-Pack parameters (6 6 6) for the cubic unit cell which consists of 24 Fe atoms and 32 O atoms. The calculated local moments for the *A*-site and *B*-site Fe atoms in the bulk Fe_3O_4 are $3.38\mu_B$ (minority spin) and $3.50\mu_B$ (majority spin), respectively, which compare well with the previous calculations.¹²

All surface systems are simulated by periodic slabs separated by vacuum. A thickness of at least 11.4 Å, i.e., 11 interlayer spacings between atomic layers along the $\text{Fe}_3\text{O}_4(001)$ direction, for vacuum is used in the simulations. A slab consisting of nine atomic planes was used in the initial simulation and a thicker slab consisting of 17 atomic planes was used to check the convergence in the thickness of the slabs. Exactly the same sizes of supercells were used for the four surface models in the two sets of calculations. The tests showed that the atomic displacements for atoms near the surface can be described quite well using the thin slabs. However, the atomic relaxation actually goes down quite deep into the slab, i.e., at least six atomic layers when counted from the surface (see Fig. 3). The relative energy changes, as due to using slabs of different thickness, are not similar for the four models either; they are much larger for the *A* and *A*-vac models than for the *B* and *B*-vac models.

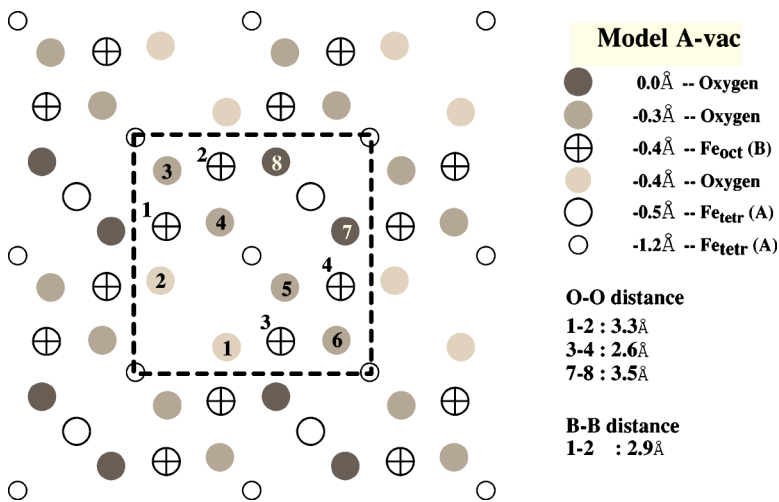


FIG. 1. The calculated relaxed structure of the A-vac model. For details please see the text.

Unless otherwise specified, the presented results are from the calculations using the thick slabs. The k -point set used in the supercells is defined by the Monkhorst-Pack parameters (6 6 2) corresponding to the same density of k points in the lateral direction as in the bulk and somewhat higher density in the film-growing direction. Relaxation processes are accomplished by moving atoms to the positions at which all atomic forces are smaller than 0.02 eV/Å.

The calculated atomic structures of the A-vac and B-vac models are presented in Figs. 1 and 2. Only atoms from the first two (B-vac) or three (A-vac) atomic layers (atomic layers according to the bulk structure, i.e., the A-type and B-type layers) are shown in the figures. The lateral positions of the atoms are plotted according to the calculated relaxed structures and the coordinates perpendicular to the surface (hereafter denoted as the z direction) are written explicitly in the figures and schematically displayed by using different sizes of symbols for A-site Fe and different degrees of darkness for oxygen atoms. The zero of the z -direction coordinate is chosen to be at the position of the outmost surface atoms. The squares with dashed borders correspond to the $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface cell.

The most surprising results in the relaxation calculations are that the outmost Fe atoms in the four considered surface models were all found to be the B-site ones. This possibility has never been conjectured in the previous studies of Fe₃O₄(001) surface structure. In fact, the A-type Fe atoms in the A and A-vac models which were originally, according to the ideal bulk-terminated positions, situated at the outmost positions moved underneath the next B-type layer following relaxation processes. Simulations using slabs of both thicknesses have led to similar results in this respect. The surface B-type layer which consists of both B-site Fe and O atoms further splits into three layers and some of the O atoms become the outmost surface atoms. For the four surface models considered here, the outmost surface atoms are always found to be O atoms. This might be due to the fact that being the outmost atoms allows O anions, which attract more valence electrons than the Fe cations, to spread out electron clouds into the vacuum to reduce kinetic energy and accordingly lower the systems' energy. The interlayer distance between the surface O layer and the second (counted from the sur-

face) A-type layer is around 1.2 Å. This is much smaller than 2.08 Å, the interlayer distance of the nearest-neighbor A-type layers in the bulk.

In the lateral direction the distances between O atoms near the surface in the A and A-vac models can deviate from that of the bulk value, i.e., 2.94 Å, as shown in Fig. 1. In the A model, the O-O distance of 1-2 and 7-8 is 3.4 Å while that of 4-5 is 3.2 Å. In the A-vac model the O-O distances, when compared to those in the A model, can be even larger, e.g., that of 7-8, due to the submerged A-site Fe, or smaller, e.g., that of 1-2, due to the Fe vacancy. In general, the O-O distances across the atomic chains of A-site Fe were found larger than that in the bulk while those across B-site Fe were smaller. Similar conclusions can be drawn for the B and B-vac models.

In the B-vac model, one notices that the interlayer distance between the surface B-site Fe layer and the next A-site Fe layer is only 0.8 Å. The same result was also found in the B model. Similar to the A and A-vac models, the surface B-type layer also split into three layers with O atoms being the outmost surface atoms. In the lateral direction the distances between O atoms can deviate much from that in the bulk due to the presence of O vacancy, e.g., the O-O distances of 1-2 and 7-1U in Fig. 2. In the B model, the O-O distance of 1-2 and 7-8 (see Fig. 1 for the whereabouts of the O atom denoted as 8) is about 3.5 Å. The O vacancy in the B-vac model can be chosen to be different from the present one, e.g., the vacancy can be due to the absence of the O atom 3 in Fig. 2 instead. However, it was found that this alternative choice is about $(0.5 \text{ eV})/(\sqrt{2} \times \sqrt{2})$ higher in energy than the present one.

In the present study we have found that the atomic relaxation plays an important role in degradation of the surface magnetic properties. To demonstrate this, we shall present the calculated results of the four surface models in the ideal structures, i.e., the bulk-terminated structures without atomic relaxation, and compare them with those of the relaxed ones. However, first we shall make a guess at how the surface magnetic properties of the ideal surface structures can be different from the bulk by assuming that the O atoms in the systems have a strong tendency to stay as O²⁻ anions. In bulk Fe₃O₄ every A-site Fe³⁺ cation provides $\frac{3}{4}$ electrons to each

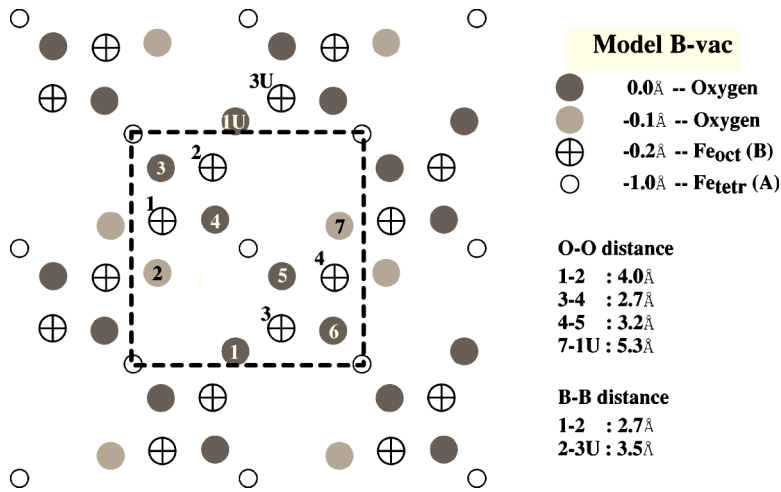


FIG. 2. The calculated relaxed structure of the *B*-vac model. For details please see the text.

of the four O atoms bonded tetrahedrally to it while every *B*-site Fe cation, which is half Fe³⁺ and half Fe²⁺, provides $\frac{5}{2} \times \frac{1}{6} = \frac{5}{12}$ electrons to each of the six O atoms bonded octahedrally to it. Every O atom in the bulk Fe₃O₄ is bonded to three *B*-site Fe and one *A*-site Fe which, according to the previous counting, makes it an O²⁻ anion.

In the *A* model, considering a $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface cell henceforth, the missing bonds for atoms near the surface can be easily identified from the ideal *A*-terminated surface. They include four O atoms for the two surface *A*-site Fe atoms ($4 \times \frac{3}{4}$), four O atoms for the four surface *B*-site Fe atoms ($4 \times \frac{5}{12}$), and four *B*-site Fe atoms for the four surface O atoms ($4 \times \frac{5}{12}$). To keep the oxygen in the system as O²⁻ anions, there are still three electrons to be distributed among the surface Fe atoms. If the three electrons are distributed only on the two surface *A*-site Fe atoms, the spin moment of the minority-spin electrons is reduced (as the *d* orbital for the *A*-site Fe³⁺ cations is already half filled) and the surface has more magnetic moments than that of the bulk. Another possibility is that the three electrons are distributed not only on the two surface *A*-site Fe atoms but also on the four surface *B*-site Fe atoms. The resulting effect will depend on how the three electrons are distributed among these six Fe atoms and the enhancement of the magnetic moment is lowered when it is compared to the previously discussed case. A similar discussion can be applied to the other three surface models and all are found to have larger magnetic moments than that of the bulk.

Qualitatively similar results were indeed obtained in our calculations for the four surface models in the ideal structures as listed in Table I. The magnetic moments of the ideal surface structures are enhanced due to surface effects and for

TABLE I. The changes in magnetic moments (positive for increase and negative for decrease) of the four surface models in the ideal and relaxed structures with respect to the calculated bulk magnetic moments. The units are μ_B per $(\sqrt{2} \times \sqrt{2})$ surface area.

	<i>A</i>	<i>A</i> -vac	<i>B</i>	<i>B</i> -vac
Ideal	+0.4	+2.0	+2.9	+2.4
Relaxed	-1.1	+0.1	-3.6	-1.8

the *A*-vac, *B*, and *B*-vac models, even the surface O atoms were observed to have non-negligible local moments of around $0.4\mu_B$. However, the enhancement of surface magnetic moments was either reversed to degradation or much reduced when atomic relaxation was allowed to take place (Table I).

In the relaxed *A* and *A*-vac models, the local moments for the submerged *A*-site Fe atoms are about $0.3\mu_B$ and $0.2\mu_B$ less than that in the bulk. However, the local moments for the surface *B*-site Fe are also reduced which results in a total of slight magnetic degradation on the surface for the *A* model and almost no surface magnetic degradation for the *A*-vac model. The lateral-plane averaged electron distribution for the *A*-vac model is shown in Fig. 3 with the indicated *z*-direction positions of the ideal (bulklike) and the relaxed *A*-site and *B*-site atoms. The magnetic polarizations of the outmost surface layer for the four relaxed models were all found to be corresponding to the majority spin as in the relaxed *A* and *A*-vac models the outmost surface Fe atoms are the *B*-site Fe atoms. In the relaxed *B*-vac model, the local

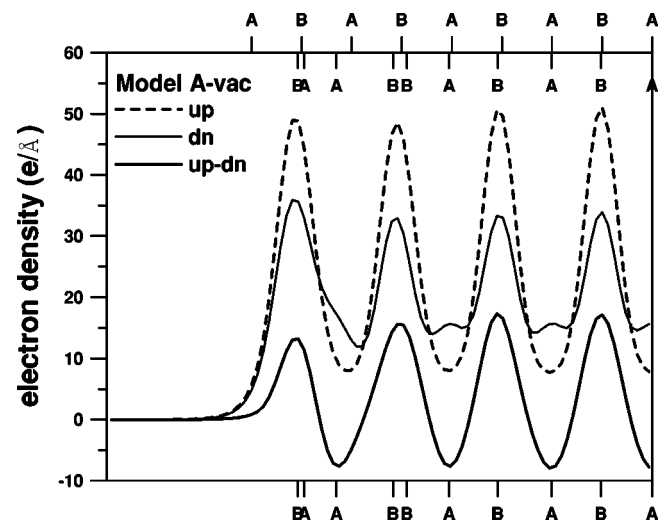


FIG. 3. The lateral-plane averaged electron distribution for the relaxed *A*-vac model. “up” and “dn” represent the majority-spin and minority-spin electrons, respectively. The ideal and relaxed atomic positions for the *A*-site and *B*-site Fe are also indicated.

moments for the surface B -site Fe atoms which are not around the O vacancy (numbers 1 and 4 in Fig. 2) were found to be about $0.9\mu_B$ lower than that in the bulk while those for the other two surface B -site Fe atoms (numbers 2 and 3 in Fig. 2) remain roughly the same as that in the bulk. In the relaxed B model, all four surface B -site Fe atoms have moments about $0.8\mu_B$ lower than that of the bulk B -site Fe. Overall, the relaxation effect is the major reason why the magnetic properties of these four surface models are degraded.

The half-metallic property of the bulk Fe_3O_4 remains for the B and B -vac models. For the A -vac model, there is no longer a gap in the density of states for the majority-spin electrons and the system is transferred to a normal metal due to the surface structure. For the A model, although the gap in the density of states for the majority-spin electrons is still there, the Fermi level is located at about 0.1 eV below the lower edge of the gap, which makes it also a normal metal.

Determination of the relative stability for the four surface models is more complicated than expected as different compositions are involved. Reuter and Scheffler¹³ have proposed a scheme for this by considering a system, e.g., the $\text{Fe}_3\text{O}_4(001)$ surface, in equilibrium with an oxygen atmosphere. The most stable surface composition is the one that minimizes the surface free energy $\gamma(T, P)$:

$$\gamma(T, P) = \frac{1}{2A} [G^{\text{slab}}(T, P, N_{\text{Fe}}, N_{\text{O}}) - N_{\text{Fe}}\mu_{\text{Fe}}(T, P) - N_{\text{O}}\mu_{\text{O}}(T, P)] \quad (1)$$

if the surface system is modeled by a slab with two equivalent surfaces and A is the area of the surface unit cell. G^{slab} is the Gibbs free energy of the slab, N_{O} and N_{Fe} are the numbers of Fe and O atoms in the supercell, while μ_{Fe} and μ_{O} are the chemical potentials of an Fe atom and an O atom, respectively. μ_{Fe} and μ_{O} are not independent if there is enough bulk material to act as a thermodynamic reservoir, i.e., $3\mu_{\text{Fe}}(T, P) + 4\mu_{\text{O}}(T, P) = g_{\text{Fe}_3\text{O}_4}^{\text{bulk}}(T, P)$, where $g_{\text{Fe}_3\text{O}_4}^{\text{bulk}}$ is the Gibbs free energy of the bulk Fe_3O_4 . The surface free energy depends now only on the oxygen chemical potential. The upper and lower limits of μ_{O} are obtained by preventing gas phase O from condensing on the sample and O atoms in the slab from leaving the sample, respectively. In the discussion

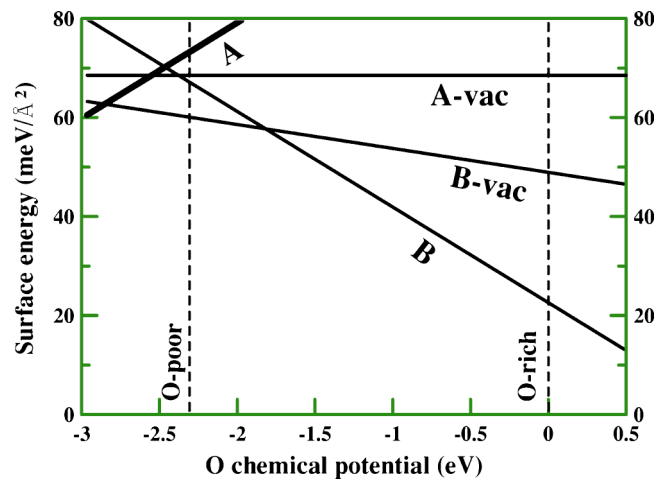


FIG. 4. Surface free energy of the four surface models. The dotted vertical lines indicate the allowed range of the oxygen chemical potential following the same approach as that of Reuter and Scheffler (Ref. 13).

of Reuter and Scheffler, a possible method of converting μ_{O} to pressure (at a fixed temperature) or temperature (at a fixed pressure) was also proposed.

We have used the same approach as proposed by Reuter and Scheffler to obtain the surface energy of the four models with respect to μ_{O} as presented in Fig. 4. The high oxygen composition of B and B -vac models is, as expected, more stable in an O-rich atmosphere. According to this scheme, the A and A -vac models are relatively less stable compared to the B and B -vac models in the allowed μ_{O} range.

In conclusion, we have shown that the A -site Fe atoms prefer to stay underneath the B -site Fe atoms in all the four surface models we considered. The degradation of magnetic properties on the surfaces was demonstrated to be due to atomic relaxations and the A and A -vac models were found to be no longer half metallic.

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*Electronic address: ccheng@phys.ncku.edu.tw

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