

Ab initio calculation on ferromagnetic reduced anatase TiO_{2-δ}Xu Zuo,^{1,a)} Soack-Dae Yoon,² Aria Yang,² Carmine Vittoria,² and Vincent G. Harris²¹College of Information Technical Science, Nankai University, Tianjin 300071, People's Republic of China²Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115, USA

(Presented on 7 November 2007; received 6 September 2007; accepted 10 January 2008; published online 19 February 2008)

The room-temperature ferromagnetism of reduced anatase (TiO_{2-δ}) is studied using density functional calculation. Two kinds of point defects, titanium interstitial and oxygen vacancy (O_v), have been studied. The calculated magnetization shows that O_v is the point defect substantially related to the observed ferromagnetism. A model of the ferromagnetism is given based on the spin-polarized Ti₃F⁺ cluster and the double exchange between the clusters. The calculated density of states supports the model and is in agreement with the donor impurity band exchange model.

© 2008 American Institute of Physics. anataseferromagnetismvacancyinterstitialab-initio calculation [DOI: 10.1063/1.2839342]

Since the discovery of the room-temperature ferromagnetism of Co-doped anatase,¹ many studies have been conducted on magnetically doped titanium dioxide. Recently, it was discovered that reduced anatase (TiO_{2-δ}) without any magnetic dopant can be ferromagnetic.^{2,3} The zero-temperature magnetization (M_s^0) is 47.7 G and the Curie temperature (T_C) is 880 K. The room-temperature carrier is *n* type and its density ($\rho_c \sim 3 \times 10^{17} \text{ cm}^{-3}$) is much lower than the spin density ($\rho_s \sim 4 \times 10^{21} \text{ cm}^{-3}$). In addition, the high magnetization is coincident with the high conductivity in the thin films deposited with the low oxygen pressure. The measurements and observations suggest that the donor defects, induced by the film-substrate lattice mismatch and the oxygen-deficient environment, may cause double exchange.² Previous *ab initio* calculation⁴ have shown that oxygen vacancy (O_v) and titanium interstitial (Ti_i) are the two most stable native point defects in oxygen-deficient anatase. However, it is still unknown which kind of defect is substantially related to the observed ferromagnetism. Also, it is still unknown how this kind of defect causes the double exchange. In this paper, we perform *ab initio* calculations on reduced anatase to answer the above two questions.

Anatase is a tetragonal phase of TiO₂ ($a=3.78 \text{ \AA}$, $c=9.51 \text{ \AA}$, space group: $I4_1/amd$). The unit cell with the O_v (or Ti_i) concentration of 1/16 is constructed by removing one O atom from (or inserting one Ti atom into) the $2 \times 1 \times 1$ supercell (Ti₈O₁₆). The unit cell with the O_v concentration of 1/32 is constructed by removing one O atom from the $2 \times 2 \times 1$ supercell (Ti₁₆O₃₂). Both atomic positions and lattice constants of the unit cells are relaxed using the VASP code with the ultrasoft pseudopotentials and generalized gradient approximation (GGA) exchange correlation. The energy convergence limit is 10^{-4} eV for the electronic loops and 10^{-3} eV for the ionic loops. The net spin-density map is also given by the VASP. The magnetization and density of states (DOS) are calculated using the WIEN2K code with the

full-potential linear augmented plane wave method and GGA exchange correlation. The energy convergence limit is 10^{-6} Ry . The error of magnetic moment is estimated using the standard deviation of the last ten steps. Spin-polarization options are enabled in all calculations.

The calculations show that either O_v or Ti_i distorts the local structure around itself (Fig. 1). In the case of relaxed O_v (Ti₈O₁₅ and Ti₁₆O₃₁), we may take the shortest distance between the Ti⁴⁺ ions around the O_v as a measure of the structural distortion (Table I).⁵ The Ti–Ti distance is increased by 4.6% in Ti₈O₁₅ and by 6.3% in Ti₁₆O₃₁. Previous *ab initio* study on the defects in HfO₂ showed that the neutral *F* center (*F*⁰ center) increases the Hf–Hf distance by 1.4% and the *F*⁺ center by 5.6%.⁵ Moreover, previous *ab initio* study on the relaxed O_v in rutile showed that the *F*⁺-center level is lower than the *F*⁰-center level.⁶ Therefore, we may infer that the *F*⁺ center forms at the O_v. In the case of non-relaxed O_v (Ti₈O₁₅-NR), following the same reasoning, we may infer that the *F*⁰ center forms at the O_v. For convenience of further discussion, we may define the Ti₃F⁺ (or Ti₃F⁰) cluster consisting of the *F*⁺ center (or the *F*⁰ center) and the three Ti⁴⁺ around it.

The calculations show that both O_v and Ti_i may induce ferromagnetism to TiO₂ (Table II). However, the O_v may induce a much stronger magnetization than the Ti_i. The mag-

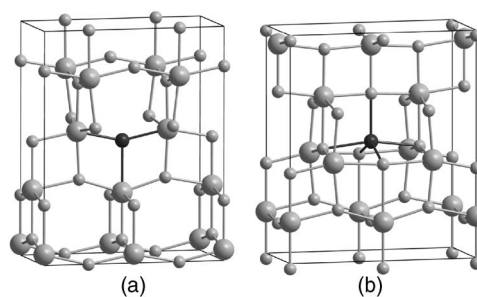


FIG. 1. The unit cells of (a) Ti₈O₁₅ and (b) Ti₁₆O₃₁ after relaxation. The big and small light balls are Ti and O atoms, respectively; the dark balls are (a) O_v and (b) Ti_i.

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TABLE I. The shortest distance between the Ti^{4+} ions around the O_v .

	$\text{Ti}_8\text{O}_{15}\text{-NR}$	Ti_8O_{15}	$\text{Ti}_{16}\text{O}_{31}$
d_{TiTi} (\AA)	3.04	3.18	3.23

netization of Ti_8O_{15} is $0.87\mu_B$ per unit cell (29 G); the magnetization of Ti_9O_{16} is $0.032\mu_B$ per unit cell (1.0 G). This result suggests that the O_v , instead of Ti_i , may be the point defect substantially related to the observed ferromagnetism. The magnetization of $\text{Ti}_8\text{O}_{15}\text{-NR}$ is $0.057\mu_B$, which is 7% of Ti_8O_{15} . This suggests that the magnetization of $\text{TiO}_{2-\delta}$ is sensitive to the local structure around the O_v . The magnetization of $\text{Ti}_{16}\text{O}_{31}$ is $0.71\mu_B$ per unit cell (12 G).

The calculated net spin-density map of Ti_8O_{15} (Fig. 2) shows that the local magnetic moment is concentrated in the Ti_3F^+ clusters, and that each Ti ion extends a lobe with high net spin density toward the F^+ center. It is possible to explain the spin polarization of the Ti_3F^+ cluster by simply using the molecular orbital theory. The molecular orbitals are formed by taking the s -like orbital of the F^+ center and the Ti d orbitals extending toward the F^+ center. Due to the local symmetry (C_{2v}), the ground state is nondegenerate. As there is only one electron in the Ti_3F^+ cluster, the ground state is spin polarized. This simple model can also explain the low magnetization of $\text{Ti}_8\text{O}_{15}\text{-NR}$. In $\text{Ti}_8\text{O}_{15}\text{-NR}$, the F^0 center forms at the O_v . As the ground state is nondegenerate, the two electrons in the Ti_3F^0 cluster form a spin singlet in the ground state. In fact, a similar model was proposed by Coey *et al.* to explain the local magnetic moment arising from the O_v in HfO_2 .⁷

The double exchange between the Ti_3F^+ clusters can be introduced naturally. When the F^+ center forms at the O_v , one electron is trapped in the F^+ center, and the other one relaxes into the conduction band, most likely the $4s$ and $3d$ bands. The conduction electrons can propagate between the Ti_3F^+ clusters. The itinerant electron aligns the spins trapped in the Ti_3F^+ clusters parallel to each other (Fig. 3). Both

TABLE II. The energy gap between the ferromagnetic and nonmagnetic states, the total magnetic moment, and the error of magnetic moment.

	$E_{\text{FM}} - E_{\text{NM}}$ (Ry)	m_t (μ_B)	err_m
Ti_9O_{16}	-9×10^{-6}	0.032	1×10^{-3}
$\text{Ti}_8\text{O}_{15}\text{-NR}$	-3.15×10^{-4}	0.057	6×10^{-4}
Ti_8O_{15}	-8.46×10^{-4}	0.87	2×10^{-2}
$\text{Ti}_{16}\text{O}_{31}$	-4.628×10^{-3}	0.71	4×10^{-4}

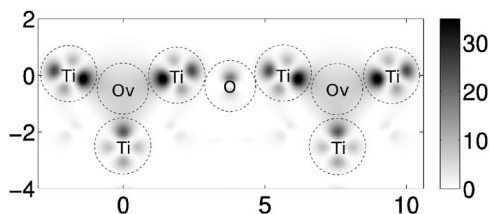


FIG. 2. The net spin-density map of the (010) plane passing through the O_v in the unit cell of Ti_8O_{15} . The dash circles are the muffin-tin spheres. The unit of the horizontal and vertical axes is \AA , and that of the color bar is number of spins per unit cell.

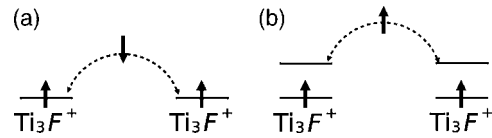


FIG. 3. The double exchange between the Ti_3F^+ clusters via (a) antiferromagnetically coupled and (b) ferromagnetically coupled itinerations.

spin-up and spin-down conduction electrons may contribute to the ferromagnetism. For spin down, the coupling is between ground states, and the conduction electrons are antiferromagnetically coupled to the localized spins. In magnetite (Fe_3O_4) above the Verwey temperature, this antiferromagnetically coupled coupling causes the ferromagnetism.⁸ For the spin up, coupling is between the low-lying excited states, and the conduction electrons are ferromagnetically coupled to the localized spins. In ferromagnetic manganite, the ferromagnetically coupled itinerant electrons cause the ferromagnetism.⁹

In the calculated systems (Ti_8O_{15} and $\text{Ti}_{16}\text{O}_{31}$), Ti_3F^+ clusters form one-dimensional chains due to the translational symmetry of the lattice. Two adjacent clusters in a chain are connected by an in-plane Ti–O–Ti bridge. This configuration enables the conduction electrons to transfer via the bended ($\sim 180^\circ$) $d_{pd}-\pi$ bond and to involve the ferromagnetically coupled itineration between the low-lying excited states of the Ti_3F^+ clusters. On the net spin-density map (Fig. 2), this transfer induces a modest spin polarization (parallel to the spins localized in the Ti_3F^+ clusters) to the O p orbital. This configuration should give a strong double exchange between two adjacent Ti_3F^+ clusters.

The calculated DOS of Ti_8O_{15} (Fig. 4) supports the above model from another viewpoint. In Fig. 4, the F^+ band corresponds to the ground state of the F^+ center, the $3d$ band corresponds to the $3d$ orbitals of the adjacent Ti ions, and the F^{++} band corresponds to the low-lying excited state of the Ti_3F^+ cluster. The spin-up F^+ and $3d$ bands are merged together, which is caused by the covalent bonding between the F^+ center and the adjacent Ti ions. The area of the merged band is ~ 1 eV, which confirms that the ground state of the Ti_3F^+ cluster is occupied by one electron. The spin-up F^{++} band is partially filled, which is caused by the ferromagnetically coupled itineration between the low-lying excited states of the Ti_3F^+ clusters [Fig. 3(b)]. The spin-down F^+ band is partially filled, which is caused by the antiferromagnetically coupled itineration [Fig. 3(a)]. The spin-down $3d$ band is almost empty. In Fig. 4, there is an obvious spin split due to

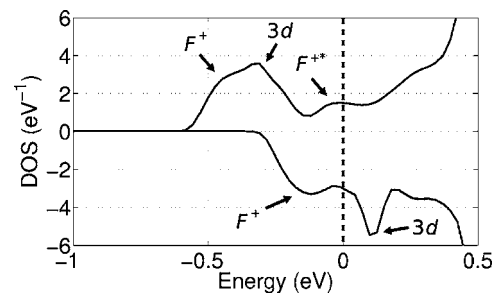


FIG. 4. The total DOS of Ti_8O_{15} around the Fermi level (0 eV).

the double exchange. The spin split of the F^+ and $3d$ bands is ~ 0.3 and ~ 0.4 eV, respectively. The larger spin split of the $3d$ band is caused by the strong double exchange between two adjacent Ti_3F^+ clusters in a chain connected by the in-plane Ti–O–Ti bridge ($dpd-\pi$ bond).

The calculated DOS of Ti_8O_{15} (Fig. 4) is in agreement with the donor impurity band exchange (DIBE) model.¹⁰ The F^+ and $3d$ bands in Fig. 4 correspond to the impurity and d bands in Fig. 4(c) of Ref. 10, respectively. The DIBE model predicts that the large spin split of the impurity band leads to high T_C . In Fig. 4, the spin splitting of the F^+ band is approximately equal to its own bandwidth. In this sense, the spin splitting of the impurity band is large and may lead to high T_C . In fact, we may estimate T_C using¹¹

$$T_C \sim U_{\text{PM}}(T_C) - U_{\text{FM}}(0),$$

where $U_{\text{PM}}(T_C)$ is the total energy of the paramagnetic phase at T_C , and $U_{\text{FM}}(0)$ is the total energy of the ferromagnetic phase at 0 K. We may use the total energy of the nonmagnetic phase as an approximation of $U_{\text{PM}}(T_C)$. Therefore, we may estimate T_C from the energy gap between the ferromagnetic and nonmagnetic states (Table II). We calculate that $T_C \sim 700$ K for $\text{Ti}_{15}\text{O}_{31}$, which is close to the experimental value.

In conclusion, we have studied the ferromagnetism of reduced anatase using *ab initio* calculation. The calculations have answered the two questions stated at the beginning. First, the O_v is the point defect substantially related to the observed ferromagnetism. Second, the formation of F^+ cen-

ters at the O_v results in the spin-polarized Ti_3F^+ clusters and the conduction electrons. The itineration of the conduction electrons between the clusters causes the ferromagnetic double exchange between the clusters. Both calculated net spin-density map and density of states support our model of the ferromagnetism. The calculated density of states is in agreement with the donor impurity band exchange model.

This research is sponsored by China National Science Foundation Grant No. 60601001 and Nankai Institute of Scientific Computing.

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