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The origin of oxygen vacancy induced ferromagnetism in undoped TiO_2

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Abstract

Using the full-potential linearized augmented plane wave method, we have investigated the oxygen vacancy defect induced ferromagnetism in both rutile and anatase TiO_2. It has been found that the oxygen vacancy induces lattice distortion in rutile TiO_2, whereas there is no such meaningful change in the anatase structure. Interestingly, the lattice distorted rutile TiO_2 shows an oxygen vacancy induced ferromagnetic state with a magnetic moment of 0.22 μ_B in the Ti atom neighboring the vacancy site, while only 0.06 μ_B is observed in the Ti atom in anatase TiO_2. We attribute the sizable magnetic moment due to the oxygen vacancy in rutile TiO_2 to the charge redistribution owing to lattice distortion. Experimentally measured magnetic hysteresis curves for undoped rutile and anatase TiO_2 films clearly display ferromagnetic behavior at room temperature. The observed magnetic strength of the rutile sample turns out to be larger than that of the anatase sample, in accordance with the theoretical calculations.

(Some figures in this article are in colour only in the electronic version)

The observation of magnetic states in Mn doped semiconductors [1] has stimulated great research interest in dilute magnetic semiconductor (DMS) use for potential spintronics device applications. Owing to the extensive studies, DMSs of various types have been found and in particular the transition metal doped wide band gap materials such as ZnO and GaN are of interest because these materials show a high critical temperature and are promising for short wavelength optical device use. In most DMSs related studies so far, it has been believed that the 3d transition metal elements are necessary for displaying the magnetic state no matter what the hosting semiconductor materials are.

One can see many magnetic semiconductors and oxide materials that display magnetic states without any d electrons like TiO_2, In_2O_3, ZnO thin films, and GaN [2–6]. This indicates that the semiconducting material can display magnetic signals even without any 3d transition metal element. For oxide materials, it is proposed that the oxygen vacancy defect may play an important role in this unexpected ferromagnetism [7–9] and, on the theory side, importance of the vacancy defect in HfO_2, $(Ti, Co)O_2$, and $(Ti, Cu)O_2$ has been suggested [10–14]. One can also find that the oxygen vacancy mediates ferromagnetism in Co doped anatase TiO_2 [15]. However, in this case the transition metal element Co exists and this may affect the magnetism of the material. Thus, the intrinsic effect of the vacancy defect on the magnetic state in undoped TiO_2 still remains an open question. In our paper, we aim to explore this issue using an *ab initio* method based on density functional theory (DFT) and to verify the theoretical prediction through an experimental observation.

We have considered TiO_2 of two types: anatase and rutile structures. The optimized atomic structure is obtained with the ultrasoft pseudopotential CASTEP package [16], using an energy cut-off of 340 eV and $3 \times 3 \times 4$ k-points. Taking advantage of these fast pseudopotential results, we transfer the optimized structure to the full-potential linearized augmented plane (FLAPW) method for considering electronic and magnetic properties. Therefore, no shape approximation is assumed in the charge, potential, and wavefunction expansions [17–19]. We treat the core electrons fully relativistically, and the spin–orbit interactions among valence electrons are dealt with second variationally [20]. The generalized gradient approximation is used to describe the

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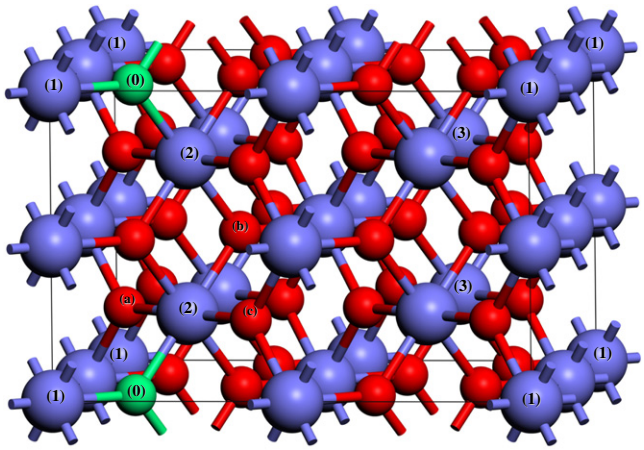

Figure 1. Model structure of rutile TiO_2 with an oxygen vacancy defect. The green ball stands for the oxygen vacancy site. The periodicity can be seen from Ti(1) atoms which are placed at the four corners of the unit cell. The larger ball stands for Ti and the smaller one denotes the oxygen atom.

exchange–correlation [21]. Spherical harmonics with $l_{max} = 8$ are used to expand the charge, potential, and wavefunctions in the muffin tin region. Energy cut-offs of 225 and 13.7 Ryd are implemented for the plane wave star function and basis expansions in the interstitial region. We use 400 k-points of the mesh during the course of the entire calculation discussed in this paper. In this paper, we will explore anatase and rutile TiO_2. The $2 \times 2 \times 2$ supercell is employed in our calculations. This corresponds to 48 atoms in an unit cell and one oxygen vacancy is present for both anatase and rutile systems.

It is realized that the optimized crystal structure of anatase TiO_2 does not significantly differ from the ideal one even in the presence of an oxygen vacancy. The lattice distortion due to the oxygen vacancy defect is at most within 0.1 Å near the vacancy site. Far from the vacancy point, the distortion is almost negligible. With this finding, we have performed FLAPW calculations for the magnetic properties and have observed that the system shows a very weak magnetic moment of 0.06 μ_B in Ti atom due to an oxygen vacancy. Although the role of the vacancy defect in $(Ti, Co)O_2$ has been presented [11], it is obvious that the magnetism is affected by the Co dopant. Thus, the interpretation may not be appropriate for revealing the origin of the ferromagnetism in undoped oxide materials. Since we have obtained a very weak magnetic state in anatase TiO_2 in the presence of oxygen vacancy, we will focus on the rutile structure in the following discussion. To explore the effect of the vacancy defect on the ferromagnetism, we have calculated the possibility of achieving a ferromagnetism arising from Ti or O vacancy defects. It is achieved when the lattice structure of rutile TiO_2 with a Ti vacancy displays more or less the same geometry as an ideal system. Besides, we have obtained a non-magnetic state. Overall, we conclude that both rutile and anatase TiO_2 are not ferromagnetic in the presence of the Ti vacancy. Now, the last structure of interest is a rutile TiO_2 with an oxygen vacancy.

In figure 1, we first present the unit cell considered in this paper. The red balls stand for oxygen atoms and the blue balls for Ti atoms. The green ball denoted by number '0' is an oxygen vacancy site that is empty in real calculations. Note that the labeled atom with the same number shown in the schematic illustration is in the same environment. Interestingly, the structure optimized using the CASTEP package shows a large lattice distortion around the oxygen vacancy position. In table 1, we present the calculated relative distances denoted by $d(ij)$ among a few representative atoms in both of lattice distorted and ideal structures, respectively. Here, i and j mean the atoms labeled in figure 1. For instance, the relative distance between Ti(1) and Ti(2) was 3.57 Å in the ideal bulk, but it changes to 3.962 Å and the distance between Ti(1) and Ti(3) has been changed from 3.57 to 3.39 Å. Comparing with anatase cases, one can see that the lattice distortion owing to an oxygen vacancy in the rutile structure is quite significant and probably observable. Indeed, the total energy calculation reveals that the distorted system is more stable by 550 meV/cell. It is well known that the magnetic properties of materials are very sensitive to change of the underlying electronic structure and the band structure is dependent on the crystal structure. Therefore, it will be of interest to explore whether the oxygen vacancy itself can cause experimentally observable ferromagnetism in oxide materials. To this end, we have calculated the effect of the vacancy defect on the magnetism without any lattice distortion and there was no indication of a magnetic state. This result suggests that the oxygen vacancy itself has nothing to do with the ferromagnetism at least in rutile TiO_2. Nonetheless, very surprisingly the FLAPW calculation shows that the distorted rutile TiO_2 manifests oxygen vacancy defect induced magnetic moments in Ti atoms. We have obtained that the oxygen vacancy induces a magnetic moment in Ti(2) and Ti(3) atoms and the calculated magnetic moments in Ti(2) and Ti(3) are about 0.22 and 0.16 μ_B, respectively. The magnitude of the magnetic moment in lattice distorted systems is quite significant compared with that in anatase TiO_2. This result implies that the structural factor owing to the vacancy defect plays an essential role in determining the magnetism of undoped TiO_2.

Table 1. Calculated distances (in Å) for both distorted and ideal structures.

	Ideal	Distorted	Difference
$d(12)$	3.570	3.962	0.392
$d(13)$	3.570	3.390	−0.180
$d(2a)$	1.949	1.950	0.001
$d(2b)$	1.949	1.824	−0.125
$d(2c)$	1.949	1.874	−0.075

In figure 2, we present the density of states (DOS) of Ti(2) and Ti(3) atoms which neighbor with oxygen vacancy sites. The green and red lines are for the DOS of Ti(2) and Ti(3) in the distorted systems, respectively, and the black lines are for Ti(2) in the ideal structure without any distortion even in the presence of the oxygen vacancy. As shown, the Ti(2) atom in the ideal structure represented by the black line shows an almost negligible magnetic moment. Interestingly, the Ti(2) and Ti(3) in the distorted structure have an asymmetric DOS due to the lattice distortion resulting in the magnetic moment in

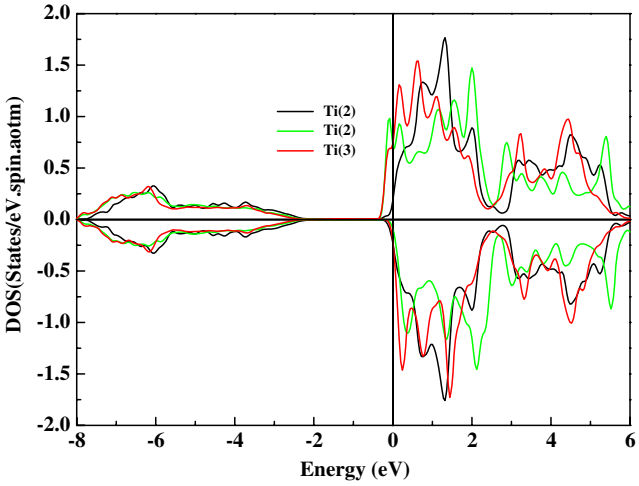

Figure 2. Calculated DOS of the magnetic Ti atoms. The green and red lines are the DOS of Ti(2) and that of Ti(3) in the distorted rutile structure, whereas the black line denotes DOS of Ti(2) in the ideal structure.

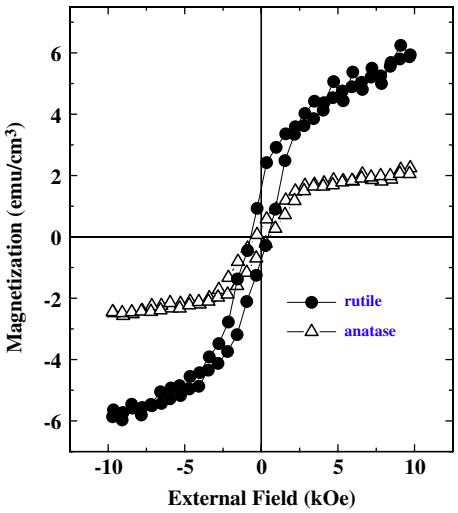

Figure 3. M–H curves for rutile and anatase TiO_2 films measured at room temperature.

these atoms. The magnetic moment is simply the difference in electron number below the Fermi level and one can see major changes in majority-spin states, while there is no meaningful change for the magnetic moment in minority-spin states. For instance, the Ti(2) atom has more electrons below the Fermi level (E_F) as compared with the ideal case. This indicates that the lattice distortion causes charge redistribution. Indeed, we have found that the Ti(2) atom in the distorted structure has about 0.1 more electrons compared with the same atom in the ideal case. One may note that E_F resides near the peak of the DOS and we believe that this results in the induced ferromagnetic state satisfying the Stoner condition. To support the *ab initio* prediction, we have also performed experimental measurements on rutile and anatase TiO_2 samples.

Thin films of rutile and anatase TiO_2 were prepared by a sol–gel method in which the precursor solution was prepared by dissolving titanium butoxide, $Ti[O(CH_2)_3CH_3]_4$, in a solvent. When 2-methoxyethanol was used as the solvent, the resultant TiO_2 films exhibited anatase structure. On the other hand, when monoethanolamine was added to 2-methoxyethanol for dissolving titanium butoxide, the resultant TiO_2 films exhibited the rutile structure. The precursor solution was stirred at 70 °C for 2 h to attain homogeneity. The substrates, $Al_2O_3(0001)$, were then spin coated with the precursor solution at 3000 rpm for 20 s to make precursor films which were then pre-heated in air at 300 °C for 5 min. This process was repeated to increase the film thickness. After the spin coating, the precursor films were annealed at 700 °C for 4 h in an evacuated chamber with the pressure of about 10^{-3} Torr. The thicknesses of the prepared anatase and rutile films measured by scanning electron microscopy were in the 600–700 nm range.

Although it is hard to estimate the density of oxygen vacancies in the films, it is believed that the vacuum annealing is likely to induce a finite amount of oxygen vacancies in the samples. Hall measurements indicate that both rutile and anatase samples exhibit n-type character with carrier concentrations (conductivities) of 3.4×10^{18} cm^{-3} (0.60 Ω^{-1} cm^{-1}) and 8.3×10^{19} cm^{-3} (6.2 Ω^{-1} cm^{-1}), respectively, at room temperature. When the precursor films were annealed in air, the resultant rutile and anatase films were found to be insulating. Thus, the observed semiconducting properties of the present vacuum annealed TiO_2 samples are believed to stem from the oxygen vacancies. The instability in Ti–O covalent bonding due to oxygen vacancy environments is likely to create mobile charges.

As shown in figure 3, the magnetization (M) versus applied magnetic field (H) curve measured by vibrating sample magnetometry at room temperature for the present vacuum annealed TiO_2 films exhibited well-defined hysteresis loops for both rutile and anatase structure, indicative of ferromagnetic properties. The observed M reaches 6 and 2 emu cm^{-3} at $H = 10$ kOe for the rutile and the anatase samples, respectively. The air annealed samples exhibited no observable M–H hysteresis behavior. One may note that the hysteresis loop of anatase TiO_2 shows very weak ferromagnetic behavior, but this is substantially enhanced in the rutile system. In other words, the influence of the oxygen vacancy defect on the magnetism is clearly noticeable in the rutile structure and this result agrees well with the *ab initio* prediction. Hong *et al* [3] reported that annealing ferromagnetic TiO_2 films (with anatase structure) in an oxygen atmosphere for a few hours could reduce its magnetic moment enormously. It was possible to turn the sample from a ferromagnetic state to a diamagnetic state by further increasing the duration of annealing. This evidence implies that the magnetism in TiO_2 is quite strongly related to the existence of oxygen vacancies. Overall, in the experimental data, the measured magnetization of the anatase sample with the higher carrier density is smaller than that of the rutile sample with the smaller carrier density. Thus, if the two samples had been made to have the same carrier (oxygen vacancy) density, the anatase sample would have had even smaller magnetization than the rutile sample as compared to the present data, leading to even better agreement with the theoretical results.

In conclusion, we have explored the oxygen vacancy defect induced ferromagnetism in TiO_2. It has been found that the crystal structure of the anatase system in the presence of oxygen vacancy defects is almost the same as that of ideal material and a very weak magnetic moment is obtained. Unlike the anatase TiO_2, the rutile system has lattice distortion due to the oxygen vacancy and the total energy calculations show that the rutile TiO_2 is more stable in the lattice distorted structure as compared with the ideal structure. Very interestingly, we have obtained that the distorted rutile TiO_2 shows an oxygen vacancy induced ferromagnetic state resulting from charge redistribution, while the ideal structure manifests no magnetic state even in the presence of oxygen vacancy defects. The magnitude of the magnetic moment in distorted rutile is nearly four times larger than that found in the anatase sample. This implies that the oxygen vacancy defect induced lattice distortion is the most essential and a key factor for the ferromagnetism. The M–H hysteresis loop measurements manifest that the oxygen vacancy defect plays an important role in the ferromagnetism of rutile TiO_2, whereas it is rather weak in the anatase structure. Overall, we conclude that the theoretical and experimental results agree very well.

Acknowledgments

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