The enhancement of ferromagnetism in Ta-doped anatase TiO$_2$ system by iron co-doping

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Abstract. The ferromagnetic properties of Ta-doped and (Ta,Fe)-doped anatase TiO$_2$ as diluted ferromagnetic materials has been studied within spin-polarized generalized gradient approximation (GGA) and GGA + $U$ method. We observed a ferromagnetic properties in Ta-doped anatase TiO$_2$, with a total magnetic moment of 1.00 $\mu_B$/supercell, which mainly arose due to Ti 3$d$ and O 2$p$ states upon $E_F$. Furthermore, the enhancement of ferromagnetism, mainly arising due to Fe 3$d$ states, in (Ta,Fe)-doped anatase TiO$_2$ was observed up to 5.00 $\mu_B$/supercell, 5 times larger than that in Ta-doped TiO$_2$. Our results confirmed the important role of Fe doping for the ferromagnetism enhancement in Ta-doped anatase TiO$_2$.

1. Introduction

Spintronics have been interesting to be investigated due to the capability of controlling spin currents, in addition to electronic charge utilization [1]. The spintronics development was motivated by the giant magnetoresistance (GMR) discovery in magnetic Fe/Cr magnetic superlattice [2] and current-induced switching due to spin transfer [3]. Hence, the spintronics have provided new fields of material physics and future applications. Regarding semiconductor-based spintronics, diluted magnetic semiconductors (DMS) have potential application in spintronic devices [4]. Because of capability to provide ferromagnetism as well as semiconductor properties, DMS have been developed by doping transition metal in small concentration [5,6]. In early development, DMSs exhibited low-temperature ferromagnetism [7–10] with the highest Curie temperature $T_C$ of 173 K found in GaMnAs [11]. Besides that, room-temperature ferromagnetism in DMS was required to realize applications in real devices [12–14].

Motivated by high-temperature ferromagnetism up to 400 K [15], several works were performed to investigate varied aspects on Co-doped anatase TiO$_2$ [16–18]. Besides that, Co-doped rutile TiO$_2$ was also found as ferromagnetic up to 400 K [19]. There was thus several works to investigate both anatase- and rutile-based TiO$_2$ doped with different transition metals (TM) [20–23]. However, the ferromagnetism in oxide DMS might exist due to the magnetic impurity clustering. The clustering around main DMS material could occur as a consequence of imperfect chemical reaction during the synthesis. Furthermore, the clustering could provide additional magnetism, which made the magnetic properties of the system became more complicated. For avoiding such effect, pentavalent TM was therefore used as the dopant in oxide DMS, such as tantalum (Ta) [24–26].
Additional doping in the pentavalent TM-doped TiO$_2$ was also performed to obtain co-doping TiO$_2$ system. Additional Nb, Al, or Cu doping in the V-doped TiO$_2$ system promoted the lower saturation magnetization of the V-doped TiO$_2$ and the decreased electrical resistivity [27]. In contrast, higher saturation magnetization was exactly observed in Co-doped and Fe-doped TiO$_2$ due to additional Nb doping followed by the reduction of their electrical resistivity values [28]. Motivated by those results, we thus investigated magnetic properties of (Ta,Fe)-doped anatase TiO$_2$ systems, to be compared with Ta-doped anatase TiO$_2$ within a first-principle calculation.

2. Computational Details
In this work, we used generalized gradient approximation [29] (GGA) + $U$ method within density-functional theory (DFT) [30–31] to calculate electronic properties of Ta-doped anatase TiO$_2$ using Quantum-ESPRESSO [32]. This software is an open source software which is able to calculate electronic properties of materials within self-consistent (SCF) calculation.

In general, SCF condition is reached when an electron density $n(r)$ in a calculation step approaches next $n(r)$ below a threshold energy. The new $n(r)$ can be obtained by [33]

$$n_{m}^{i+1} = n_{m}^{i} + \beta R[n_{m}^{i}]$$

with $n_{m}^{i}$ and $n_{m}^{i+1}$ are electron density in $i$th-step and next step $(i + 1)$, $\beta$ is a mixing parameter and $R[n_{m}^{i}]$ is an electron density residual vector. Therefore, in a step of calculation, new optimal electron density input can be obtained as a linear combination of previous electron densities based on Pulay mixing [34]. The new $n(r)$ can be therefore described as

$$n_{m}^{i+1} = \sum_{i} \alpha_{i} \left( n_{m}^{i} + \beta R[n_{m}^{i}] \right)$$

with $\alpha_{i}$ is a coefficient given for each $n(r)$ in $i$th-step under a condition

$$\sum_{i} \alpha_{i} = 1$$

In general, the calculation is initiated by determining ultrasoft (US) pseudopotentials (PP), followed by the definition of $n(r)$. The next step is Hartree potential $V_{H}$ and exchange-correlation potential $V_{XC}$ calculation forming effective potential [35]

$$V_{eff}(\vec{r}) = V_{mcl}(\vec{r}) + V_{H}(\vec{r}) + V_{XC}(\vec{r})$$

then, equation (1) can be solved using Schrödinger equation

$$\left( -\frac{1}{2} \nabla^{2} + V_{eff}(\vec{r}) \right) \psi_{i}(\vec{r}) = \varepsilon_{i} \psi_{i}(\vec{r})$$

with electron density

$$n = \sum_{i} |\psi_{i}(\vec{r})|^{2}$$

Inputs included in the calculation are Bravais lattice type, $k$-point mesh, atomic positions, lattice parameters, kinetic energy cutoff, and Hubbard-$U$ corrections. Our models are $2 \times 2 \times 2$ supercells of Ti$_{1-x}$Ta$_{x}$O$_2$ and Ti$_{1-x-y}$Ta$_{x}$Fe$_{y}$O$_2$ structures ($x = y = 3.125\%$) in I4$_1$/amd space group [36]. The Ta and Fe
dopants were put at coordinates of (1/2 1/2 1/2) and (1/2 3/4 5/8) to realize two nearest-neighboring O ions sharing. The optimized tetragonal lattice parameters are $a = b = 7.92$ Å and $c = 19.10$ Å. Pseudopotentials (PP) used in this calculation are basically formed by plane wavefunctions (PW). Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional type was used in the calculation [29]. Besides, we used a Γ-centered $k$-point mesh of $2 \times 2 \times 2$ and a cut-off kinetic energy of 544 eV. Threshold force in structure optimization was 0.514 eV/Å based on Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization algorithm [37–40]. We used $U_{eff}$ ($U - J$) potential energy of 5.8 eV, 3.0 eV, and 5.9 eV for Ti 3$d$, Ta 5$d$, and Fe 3$d$ orbitals based on previous works [41,42]. In general, electrons in the valence states (weakly-bonded electrons) of each atom are involved, i.e Ti (3$p^63d^24s^2$), Ta(5$p^65d^36s^2$), O(2$s^22p^4$), and Fe(3$p^63d^64s^2$), while electrons in the remaining inner orbitals were assumed to be strongly bonded as core states.

3. Results and Discussions
Firstly, we investigated magnetic properties of anatase Ta-doped and (Ta,Fe)-doped anatase TiO$_2$ using calculated total density of states (DOS) as a function of energy relative to Fermi level, as shown in Figure 1.

Figure 1. Calculated spin-dependent total DOS of (a) Ta-doped and (b) (Ta,Fe)-doped anatase TiO$_2$.

In general, both DOS graphs in Figure 1 have a similar symmetrical shape for the spin-up and spin-down electron states. However, Figure 1(a) show a small-range asymmetric DOS curve found around the Fermi level arising ferromagnetism of the Ta-doped anatase TiO$_2$. We obtain a total magnetic moment of 1.00 $\mu_B$/supercell on this system. The total magnetic moment of the Ta-doped anatase TiO$_2$ is similar with that was indicated by the previous theoretical study [43]. Besides that, Figure 1(b), a small-range asymmetric DOS curve found in an energy range of $-10.12$ to $-9.12$ eV arising ferromagnetism of the (Ta,Fe)-doped anatase TiO$_2$. We obtain a total magnetic moment of 5.00 $\mu_B$/supercell for this system, namely about 5 times larger than that of Ta-doped anatase TiO$_2$.

In order to observe a detailed ferromagnetic mechanism of both systems, we plotted projected-DOS (PDOS) as a function of energy relative to the Fermi level, as shown in Figure 2. Based on Figure 2(a), we observed that ferromagnetism in the Ta-doped anatase TiO$_2$ mainly arises due to observed hybridization between spin-up Ti 3$d$ and O 2$p$ states upon the Fermi level. The hybridization was supported by the previous theoretical result [43] which shows that instead of Ta 3$d$ states, some spin-up Ti 3$d$ states exactly lie upon the Fermi level. The largest local magnetic moment at four Ti ions, where each Ti ion has a local magnetic moment of 0.31 $\mu_B$, as shown in Table 1. Otherwise, Ta 5$d$ states remain to provide a small contribution to ferromagnetism. This small contribution is also indicated by a small local magnetic moment at Ta ion of 0.05 $\mu_B$, as shown in Table 1. The mechanism of magnetism can be
described as follows. Since the Ta atom has three electrons at 3d orbital, there is one electron remaining after the Ta atom is ionized (Ta$^{5+}$). Based on our results, the remaining electron is dominantly shared among four nearest Ti ions. This mechanism has been also previously proposed [43]. Therefore, our Ta-doped anatase TiO$_2$ is reliable for Fe co-doping.

**Table 1.** Local magnetic moments of Ta ion and its two nearest Ti ions.

| Ions | Coordinate | Site symmetry | Wyckoff letter | Local magnetic moment (μB) |
|------|------------|---------------|----------------|---------------------------|
| Ta   | 1/2 1/2 1/2 | .2/m.         | c              | 0.05                      |
| Ti   | 0 1/2 1/2   | .2/m.         | d              | 0.31                      |
|      | 1/2 0 1/2   | .2/m.         | c              | 0.31                      |
|      | 1 1/2 1/2   | .2/m.         | d              | 0.31                      |
|      | 1/2 1 1/2   | .2/m.         | c              | 0.31                      |

**Figure 2.** Calculated spin-dependent PDOS (a) of Ta-doped and (b) (Ta,Fe)-doped anatase TiO$_2$.

**Figure 3.** Schematic illustration of local magnetic moments of Ta, Fe, and nearest-neighboring O ions in the (Ta,Fe)-doped anatase TiO$_2$. 
Furthermore, different ferromagnetism mechanism is observed in Figure 2(b). The two peaks in small-range spin-up states are found to be largely dominated by Fe 3$d$ states hybridized with O 2$p$ states. Moreover, we found a large local magnetic moment at the Fe ion of 4.261 $\mu_B$ in the (Ta,Fe)-doped anatase TiO$_2$ leading to the total magnetic moment of 5.00 $\mu_B$, as shown in Figure 3. Otherwise, a small local magnetic moment of 0.007 $\mu_B$ at the Ta ion is observed. Based on Figure 3, there are two O ions which are shared among the Fe and Ta ions. Both shared O ions are polarized up to 0.074 $\mu_B$ and 0.075 $\mu_B$ (noticed with green letters). The upper O ions have higher local magnetic moments, where the top O ion has a local magnetic moment of 0.128 $\mu_B$. In contrast, the lower O ions, which are also the nearest neighbors of the Ta ion, almost have no local magnetic moments. Based on the analysis, the large ferromagnetism in the (Ta,Fe)-doped anatase TiO$_2$ is exactly induced by the Fe co-dopant.

4. Conclusions
We observe ferromagnetism in anatase Ta-doped anatase TiO$_2$, with the total magnetic moment of 1.00 $\mu_B$/supercell, which mainly arise due to Ti 3$d$ states hybridized with O 2$p$ states upon $E_F$. The enhancement of ferromagnetism is observed in the (Ta,Fe)-doped anatase TiO$_2$, which mainly arises due to Fe 3$d$ states hybridized with O 2$p$ states. The total magnetic moment the (Ta,Fe)-doped anatase TiO$_2$ is 5.00 $\mu_B$/supercell. Therefore, the high ferromagnetism observed in the (Ta,Fe)-doped anatase TiO$_2$ provides potential DMS application.

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