The Electronic Structures and Magnetic Properties in Ti-doped MgO

Yifei Chen, Qinggong Song, Huiyu Yan and Yanrui Guo

College of Science, Civil Aviation University of China, Tianjin, 300300, People's
Republic of China
Email: yifei_chen@163.com

Abstract. Using first-principles calculations based on density functional theory, we
investigated systematically the electronic structures and magnetic properties of Ti monodoping
and (Ti, Mg vacancy) codoping in MgO. The results indicate that a single Ti substitution of Mg
prefers the ferromagnetic ground state and behaves a metallic character. In addition, it has been
found that the two Ti dopants favor AFM coupling in the near configuration, whereas the FM
state is more stable in the far configuration. Interestingly, the FM stability can be evidently
intensified by introducing Mg vacancy. The magnetic moment mainly comes from the spin
polarized Ti $3d$ and O $2p$ electrons which can be explained in terms of p-d hybridization
mechanism and room temperature ferromagnetism can be expected. Furthermore, the doped Ti
atoms in the MgO host have no clustering tendency. These results suggest that the Ti-doped
MgO is a promising candidate material for room temperature spintronics applications.

1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted considerable attention because they hold the
promise of using electron spin, in addition to its charge, in creating a new class of spintronic
semiconductor devices that combine the function of information processing and storage [1]. The ideal
DMSs should exhibit ferromagnetism at room temperature for practical applications and have a
homogeneous distribution of the magnetic dopants. Since Dietl et al. theoretically predicted that room
temperature (RT) ferromagnetism might exist in wide-band-gap semiconductors [2], a number of
transition metal (TM) doped semiconductors indeed detected RT ferromagnetism, such as TM-doped
TiO_2 [3], In_2O_3 [4], SnO_2 [5], ZnO [6] and MgO [7]. Much effort has been devoted to study the nature
of ferromagnetism, aiming at designing ferromagnetic DMS materials with RT ferromagnetism.
However, a number of studies indicate that the RT ferromagnetism may come from precipitation of
magnetic clusters or from the secondary magnetic phases and no convincing evidence can verify that
the observed ferromagnetism is intrinsic. These extrinsic magnetic behaviors are undesirable for
practical application. Up to now, the origin of ferromagnetism in oxide DMSs is still unclear.

Recently, a new class of oxide ferromagnets has arisen, bringing new challenges for the
understanding of the underlying physics of long-range ferromagnetic ordering in oxide compounds [8-
17]. In these systems, the ferromagnetic behavior is driven by native defects and therefore there are no
complications arising from additional phases or clustering effects induced by the doping process, thus
they are considered as promising spintronic materials. However, the origin of the magnetism remains
to be clarified.

MgO has recently attracted a great deal of attention as a promising material to understand the
magnetic mechanism of oxide ferromagnets. If MgO is made ferromagnetic via dilute magnetic doping,
it may also work as a spin filter or induce a large magnetic-field effect. Besides that, Mg is an

abundant mineral in the earth therefore the magnetic oxides based on MgO would be low cost and promising primary materials, which makes it a good model system to study defect-induced magnetic properties. Recently, numerous theoretical and experimental works have proposed that Mg vacancies can induce room temperature ferromagnetism in MgO [18-20]. However, Mishra et al. reported that oxygen vacancies are largely responsible for the RT ferromagnetism in MgO [21]. Although there is a consensus that the ferromagnetism is related with native defects, considerable controversy on the origin of the magnetism still exists. Since neither Ti nor its oxides are ferromagnetic, therefore, Ti is one of the best doping elements to avoid controversies of ferromagnetism. Up till now, however, there are no related reports on ferromagnetism in Ti-doped MgO.

In this work, we investigated systematically the electronic structures and magnetic properties in Ti monodoping and (Ti, Mg vacancy) codoping in MgO by means of the first-principles calculations in the framework of the density functional theory. We found that a single Ti substitution of Mg prefers a ferromagnetic ground state and a metallic behavior. In addition, it has also been that the FM stability can be evidently intensified by introducing Mg vacancy. The mechanism of ferromagnetism is discussed.

2. Computational methods

Total energy and electronic structure calculations were performed with the Cambridge serial total energy package (CASTEP) code, which is based on density functional theory (DFT) using ultrasoft pseudopotentials [22] and a plane-wave expansion of the wave function [23]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof scheme [24] is used to treat the exchange and correlation potential. The valence-electron configurations for the O, Mg and Ti atoms were chosen as $2s^2 2p^4$, $2p^6 3s^2$ and $3s^2 3p^6 3d^2 4s^2$, respectively. The electron wave function was expanded in plane waves with a cutoff energy of 500 eV, and a Monkhorst-Pack grid [25] with parameters of $2\times2\times2$ was used for irreducible Brillouin zone sampling. The crystal structure and the atomic coordinates were fully relaxed without any restriction using the Broyden-Fletcher-Goldfarb-Shanno method [26]. In the geometry optimization process, the energy changes, as well as the maximum tolerances of the force, stress, and displacement were set as 5×10^{-6} eV/atom, 0.01eV/Å, 0.02 GPa, and 0.0005 Å, respectively.

The optimized lattice parameter is 4.286 Å, which is accordant with the experimental value of 4.213 Å [27], which indicates that the calculation models and parameters are reasonable. To study the electronic structures and magnetic properties of Ti-doped MgO, a $2\times2\times2$ supercell of MgO containing 64 atoms was constructed. For the Ti monodoping in MgO system, two doping concentrations were checked; for 3.125% doping concentrations, only one Mg atom was substituted by Ti, while for 6.25%, two Mg atoms were substituted.

3. Results and discussion

For 3.125% concentration of Ti doping, we substituted one Mg atom with one Ti atom in the $2\times2\times2$ supercell of MgO to create a research model ($Mg_{31}TiO_{32}$). The calculated total energy of the spinpolarized state is 880 meV, lower than that of the non-spinpolarized state, which indicates that a single Ti substitution of Mg prefers the ferromagnetic ground state. Fig. 1 shows the calculated band structure of MgO doped with 3.125% of Ti. One can see that a metallic behavior is shown with the Fermi energy pass through both up spin (figure 1(a)) and down spin (figure 1(b)) channels. One can also see that the impurity band merges with the conduction band at higher carrier concentrations and Ti dopant acts as a donor in MgO. Obviously, the magnetic moment comes mostly from Ti dopant in Ti-doped MgO system. This is very similar to the result of Ti doped in ZnO reported by Xiong et al. [28].

In $Mg_{31}TiO_{32}$, we have observed the spin polarized Ti atom, but it is not clear to claim the Ti-doped MgO induced ferromagnetism at this stage because ferromagnetism requires a long range magnetic interaction between magnetic atoms. It is thus necessary to have at least two Ti dopants if one wants to investigate the possibility of Ti induced ferromagnetism in MgO. For this purpose, two Mg atoms were substituted with Ti atoms, which give a dopant concentration of 6.25% and allows for calculation of the relative energies of ferromagnetic (FM) and antiferromagnetic (AFM) orderings. In this work, two spatial arrangements were explored. One is defined as the "near" configuration, where the two Mg

atoms are separated by a single O atom; another one is defined as the "far" configuration, where two Mg atoms are separated by -O-Mg-O-, as shown in figure 2. Ferromagnetic stability is determined by the total energy difference of the supercell between antiferromagnetic (AFM) and ferromagnetic (FM) configuration ($\Delta E = E_{AFM} - E_{FM}$). If ΔE is negative, the AFM configuration is more stable; and if ΔE is positive, the FM configuration is more stable. The calculated results indicate that the antiferromagnetic state is favored over the ferromagnetic one ($\Delta E = -31$ meV) in the "near" configuration whereas the ferromagnetic state has the lower energy ($\Delta E = 17$ meV) in the "far" case.
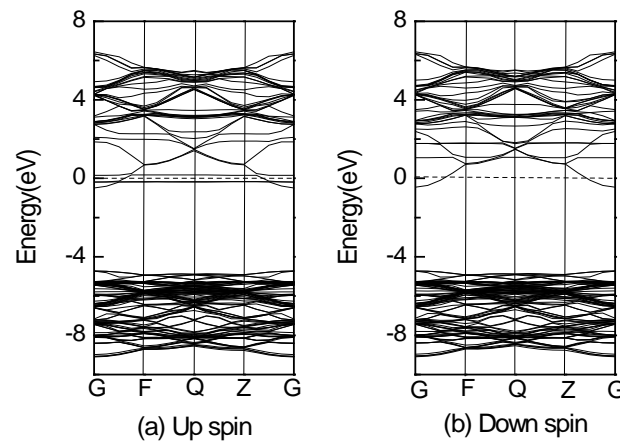

Figure 1. Band structures of the up spin (a) and the down spin (b) of MgO doped with 3.125% of Ti. Fermi level is set to zero.
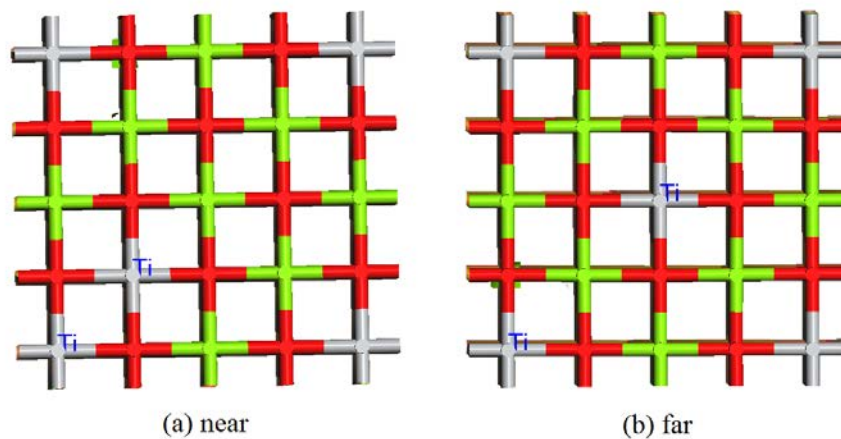

Figure 2. (Color online) Schematic illustration of 2×2×2 supercell MgO with 6.25% Ti dopant in the near (a) and far (b) arrangements, where green balls, red balls and gray balls stand for Mg, O and dopant Ti, respectively.
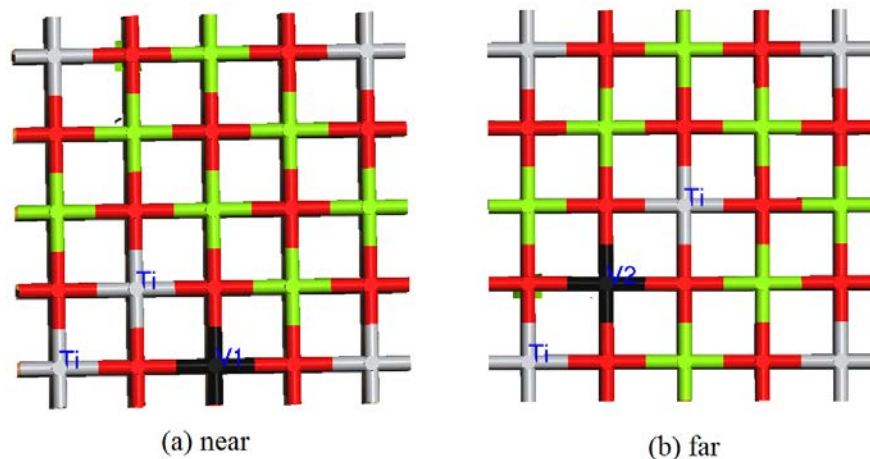
Figure 3. (Color online) Schematic illustration of 2×2×2 supercell MgO with 6.25% Ti dopant, in which a Mg atom was removed in the near (a) and far (b) arrangements, respectively; where green balls, red balls and gray balls stand for Mg, O and dopant Ti, respectively. The single Mg vacancy was labeled by V.

Codoping was viewed as a potential means to specify the availability of carriers to mediate ferromagnetism. Recently, Sundaresan et al. reported that defect induced room temperature ferromagnetism in MgO nanoparticles and attributed the ferromagnetism to Mg vacancies or Mg vacancy clusters [11]. To explore the effect of Mg vacancy on the electronic structures and magnetic properties in Ti doped MgO, one Mg vacancy was created by removing one Mg atom in the 2×2×2 supercell of MgO, as shown in figure 3. In order to determine whether the defective systems are order magnetically or not, the total energy of ferromagnetic and antiferromagnetic arrangements were calculated. The calculated results indicate that FM is ground state with a magnetic moment of 2 μB per supercell in each of the two configurations, and the total energy of the FM state is 154 and 480 meV lower than that of the corresponding AFM state for near and far configuration, respectively. Furthermore, the calculated results also indicated that the near configuration has larger total energy than the far configuration. This indicates that the two doped Ti atoms have no tendency of clustering. It is well known that the energy associated with thermal electronic fluctuations is in the order of KBT, which is approximately equal to 26 meV for T = 300 K. Therefore, RT ferromagnetism for the defective system of Ti-doped in MgO with Mg vacancy should be achieved.
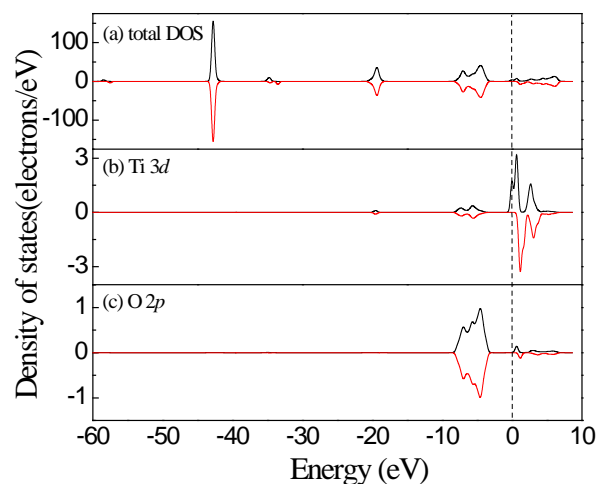

Figure 4. The total DOS and partial DOS for the $Mg_{29}Ti_2O_{32}$ defective system. The positive (negative) channel represents the up (down) spin, respectively. The Fermi level is set to 0 eV

To study the contribution of different atoms in this system for ferromagnetism, the total density of states (DOS) and partial DOS of the Mg29Ti2O32 defective system were calculated. figure 4 presents the total DOS and partial DOS of the far configuration. One can see that the Ti 3d states (figure 4(b)) overlap obviously with those of O 2p (figure 4(c)) near the Fermi level, suggesting a strong exchange interaction between them. It is the strong exchange interaction that results in the splitting of the energy levels near the Fermi energy. And thus the down spin states are fully occupied while up spin states are partially filled (figure 4(a)), which resulting in a magnetic moment of 2 μB per supercell. The local moment at Ti is about 1.68 μB and the rest magnetic moment comes from the spin polarized O atoms. This fact reveals that the ferromagnetism of the system arises from the unpaired 3d electrons of Ti and 2p electrons of O atoms. Therefore, the ferromagnetism in Ti-doped MgO should be attributed to the p-d exchange mechanism. It is the spin polarized O atoms that mediate the ferromagnetic exchange interaction between the two Ti atoms.
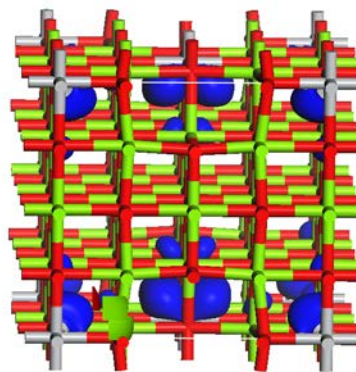

Figure 5. (Color online) A 3D iso-surface of the average spin charge density of 0.005 e/Å^3 for $Mg_{29}Ti_2O_{32}$, where green balls, red balls and gray balls stand for Mg, O and dopant Ti, respectively. Blue shells represent the 3D iso-surface.

Figure 5 presents a three-dimensional (3D) iso-surface of the average spin charge density of 0.005 e/Å^3 for the Ti-doped in MgO system associated with one Mg vacancies in a 64-atom supercell. One can conclude that the spin polarized Ti atoms is responsible for the ferromagnetism in Ti-doped MgO and the spin density on Ti atoms comes from the unpaired 3d electrons of Ti. In addition, our calculation results also indicate that Mg vacancy has no contribution to the total magnetic moment directly, combining with Mg vacancy is an acceptor defect and it can introduce holes in the defective system of Ti-doped MgO. Therefore, one can think that the additional holes induced by creating Mg vacancy are responsible for the enhancement of FM stability in Ti doped MgO.

4. Conclusions
In summary, the electronic structures and magnetic properties of Ti-monodoping and (Ti, Mg vacancy)-codoping in MgO have been investigated systematically by using first-principles calculations based on DFT. The calculated results indicate that a single Ti substitution of Mg prefers the ferromagnetic ground state and behaves a metallic character. In addition, the calculated results also indicate that the two Ti dopants favor AFM coupling in the near configuration, whereas the FM state is more stable in the far configuration. Interestingly, the FM stability can be evidently intensified by introducing Mg vacancy. The magnetic moment was mainly contributed by unpaired Ti 3d and O 2p electrons and the ferromagnetism can be attributed to the p-d hybridization mechanism. Room temperature ferromagnetism can be expected due to a large energy differences between the FM and AFM state for the defective system of Ti-doped in MgO with Mg vacancy, furthermore, the doped Ti atoms in the MgO host have no clustering tendency.

6. References

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