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The role of transition metal impurities and oxygen vacancies in the formation of ferromagnetism in Co-doped TiO_2

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Abstract

We have investigated the role of transition metal impurities and oxygen vacancies in the formation of ferromagnetism in Co-doped TiO_2 using the LSDA + U approach which takes into account strong on-site Coulomb correlations for electronic structure calculations. Several model supercells of rutile TiO_2, with a Co^{2+} ion in high-spin state substituted into the titanium site and with oxygen vacancies, were considered. We found that the exchange interaction of Co magnetic ions is ferromagnetic, but very weak due to the large average impurity–impurity distance. However, it becomes three times stronger when there is a magnetic vacancy nearby. The magnetic moment values are 3 μ_B for Co^{2+} and -1 μ_B for vacancy. Our investigation showed that the exchange interaction energy of Co and vacancy moments varies from 330 to 40 meV depending on the distance between them in the supercell. We assume that the strong interaction between Co and vacancy moments should be taken into account to explain the high Curie temperature value in Co-doped TiO_2.

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

1. Introduction

Diluted magnetic semiconductors (DMSs) have been studied extensively because of the potential possibility to use both charge and spin degrees of freedom of carriers in electronic

devices, namely in spintronics [1, 2]. However, the most investigated II–VI and III–V compounds doped with magnetic transition metal ions have a Curie temperature (T_C) of about 110 K or less.

Recent research effort has been focused on developing new ferromagnetic semiconductors operating at room temperature. Oxide semiconductors, therefore, became the subject of intense interest [2–4]. In 2001 Matsumoto *et al* [5] reported that Co-doped anatase TiO_2 can keep ferromagnetic order up to 400 K with a magnetic moment of about 0.32 μ_B/Co for a Co concentration up to 8%. More recently, Park *et al* [6] have successfully grown ferromagnetic Co-doped rutile TiO_2 films. The Curie temperature was estimated to be above 400 K for 12% of the Co content. To date, many other semiconductors showing room-temperature ferromagnetism have been fabricated [2, 3, 7].

Despite recent experimental success, there is no consistent theoretical description of DMSs. At first, ferromagnetism in Co-doped TiO_2 was explained in terms of a carrier induced mechanism like in III–V based DMSs [8]. Samples fabricated under oxygen-rich conditions show negligible magnetization and are insulators [9, 10], so one can assume that oxygen vacancies, which are easily formed in thin films, are essential to ferromagnetic order and conductivity. The magnetic moment value also depends on the sample growth conditions. For example, it is reported to be 1.26 μ_B/Co in [11], compared with the value of 0.32 μ_B/Co obtained by Matsumoto *et al* [5]. The most recent measurements [12] yield a spontaneous magnetization value of 1.1 μ_B/Co atom for the films which were highly insulating with Co in the 2+ state.

The problem of the role of magnetic ion doping and oxygen deficiency in the origin of room-temperature ferromagnetism has been considered in many theoretical papers. For example, in [13, 14] first-principles calculations were performed to consider the influence of vacancy position on the magnetic properties of Co-doped TiO_2, in particular, on the Co spin state. Park *et al* [13] treated an oxygen vacancy in the supercell ($Ti_{15}Co_1O_{31}$) by the LSDA + U method with spin–orbit coupling. They showed that for the anatase structure of $Ti_{1-x}Co_xO_2$ ($x = 0.0625$ and 0.125) the presence of an oxygen vacancy near Co results in a state with a spin magnetic moment of 2.53 μ_B, whereas the presence of a vacancy near Ti does not affect the magnetic moment value significantly. However, according to their results, an oxygen vacancy near a Ti site is more stable. This conflicts with [14], where the opposite is claimed: the oxygen vacancy prefers to stay near Co, and it causes the magnetic moment on Co to equal 0.90 μ_B. In [4], an overlap polaron model caused by shallow donor electrons was proposed to explain the high Curie temperatures in Co-doped TiO_2. Unlike super-exchange or double-exchange interaction, ferromagnetic exchange is suggested to produce long-range order. The other recent theoretical works are devoted to the role of interstitial Co that might appear in the material [15, 16]. From one point of view, interstitial Co destroys the spin polarization of the substitutional Co nearby and, hence, reduces the average impurity magnetic moment [15]. From the other results, there is an enhancement of the average value of the local magnetic moment relative to the Co^{2+} low spin state with the presence of substitutional Co [16]. Some theoretical investigations claimed that Co impurities have a strong tendency for clusterization [15, 17]. The process of preparation and the concentrations of Co impurity can lead to Co metal clusters and/or dispersed Co-matrices [18].

At the same time, the authors of [5, 9, 11] confirm the absence of Co metal clusters. Thus, there are many aspects of the physical properties of Co-doped TiO_2 which are currently under debate.

The main purpose of this work was to clarify the role of Co impurities and oxygen deficiency in the origin of ferromagnetism with high T_C in Co-doped TiO_2. Since the tetravalent Ti^{4+} ion is substituted by divalent Co^{2+}, there are intrinsic oxygen vacancies in the doped

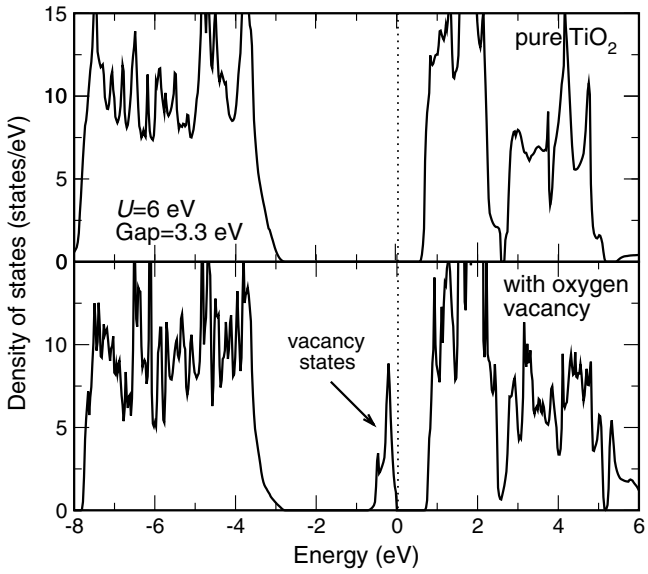

Figure 1. Total densities of states obtained from the LSDA + U calculation for pure TiO_2 (top panel) and model oxygen deficient $TiO_{2-1/4}$ (bottom panel) compounds. The figures were aligned by the edge of the oxygen bands. Zero of energy is at the top of the vacancy band for $TiO_{2-1/4}$.

system to compensate this charge difference. The actual value of oxygen deficiency is difficult to estimate because defect concentration strongly depends on the growth conditions. We have considered several model systems with various contents of Co impurity ions and vacancies. In our study we assumed that there is no Co clustering, Co ions are substitutional and their valency state is +2. Our investigations were performed using the linearized muffin-tin orbital (LMTO) band structure calculation method within the local spin density approximation with the on-site Coulomb repulsion U (LSDA + U) [19, 20]. The lattice relaxation was neglected.

The analysis was started with calculation of the electronic structure of TiO_2 in a stoichiometric case without doping and defects. TiO_2 has three kinds of crystal structure: rutile, anatase and brookite. For our calculations we chose the first one with crystallographic parameters, taken from [21]. The radii of MT spheres for LMTO calculations were $R_{Ti} = 2.42$ a.u. and $R_O = 1.85$ a.u.; two types of empty spheres (atomic spheres with zero nuclear charge) were added. The valence band is formed by mainly oxygen 2p orbitals contribution, and the conduction band by Ti 3d orbitals. The LDA calculation gave the value of band gap equal to 1.7 eV which is significantly less than the experimental value of 3.1 eV [5]. Mo *et al* [22] showed that while LDA underestimates the energy gap, other ground state properties such as equilibrium lattice constants and bulk moduli are in good agreement with experimental data. It is a well known problem of band gap underestimation in the LDA approach, where the potential is orbital-independent. It can be improved by means of the LSDA + U method, where orbital-dependent potential acts in a different way on the occupied and unoccupied d-orbitals [20]. In the top panel of figure 1, the electronic structure obtained from the LSDA + U calculation is shown. The values of on-site Coulomb interaction parameters U and J_H for Ti 3d orbitals were chosen to be 6.0 and 0.7 eV, respectively [20]. The calculated band gap value is 3.3 eV, in good agreement with the experimental value. The LMTO radii and U and J_H values were taken to provide an experimental gap value, they weakly influence the magnetic properties.

Below we present the results of our LSDA + U calculations for model systems corresponding to (1) Co impurities in TiO_2 without oxygen deficiency (section 2), (2) oxygen deficient TiO_2 but without Co impurities (section 3) and (3) the simultaneous presence of Co impurities and oxygen vacancies in TiO_2 (section 4).

The oxygen vacancies play a dual role in this material. In the first, every vacancy adds two electrons to the system and in the second, it produces localized states in the energy gap. In order to separate the influence of those factors on the electronic structure and magnetic state of the system we imitated the first one in the calculation by adding electrons to the supercell which compensated for their negative charge by the opposite sign charge being distributed over the supercell. This means we take into account the presence of the vacancy in the crystal, but somewhere far away from the atoms considered in the model calculations so that one can neglect the influence of the localized states produced by this vacancy.

The substitution of a tetravalent Ti^{4+} ion by divalent Co^{2+} has the effect of adding two holes to the system. This could also be imitated in our calculations by removing two electrons from the supercell and adding an equal uniform charge of the opposite sign. This adding (removing) of electrons is not simply a shift of Fermi energy level, as in the 'rigid band' approximation, because we performed fully self-consistent calculations with the changed number of electrons and took into account the change of the charge density distribution and hence electron potential.

In the present study we adjusted the total number of electrons in the system so that Co ions were always in the divalent state (experimental works report [9, 11, 23] that all Co ions are in the +2 formal oxidation state). In each model calculation with Co impurity the supercell of TiO_2 was considered to make the impurity concentration close to the experimental value of 8–12%. For vacancy states we have considered all three possible configurations: unoccupied, occupied with one electron and fully occupied with two electrons.

2. Cobalt-doped titanium dioxide

To investigate the electronic structure of Co-doped TiO_2, we used a supercell containing sixteen TiO_2 formula units with two Ti replaced by Co where impurities are separated by 6.59 Å. Such a supercell corresponds to 12.5% of Co content.

In order to reproduce Co ions in the +2 formal oxidation state Co^{2+} (according to experimental evidence [9, 11, 23]) we added two electrons, per Co ion, to the system (four electrons per supercell). Physically, that is equivalent to considering the system with one oxygen vacancy per Co ion ($Co_{1/8}Ti_{1-1/8}O_{2-1/8}$ instead of $Co_{1/8}Ti_{1-1/8}O_2$ model compound) but without explicitly taking into account the localized states produced by the vacancy in the energy gap.

The resulting density of states has an insulating character. In figure 2, we present the electronic structure for the $Co_{1/8}Ti_{1-1/8}O_2$ model compound obtained from the LSDA + U band calculations. The values of on-site Coulomb interaction parameters U and J_H for Co 3d orbitals were chosen as 8 and 1 eV, respectively [20].

Because of large distances between impurities due to low Co concentration, one can expect that the exchange interaction between Co ions is weak. To estimate the exchange interaction parameter, we examined the total energy difference between ferromagnetic (FM) and antiferromagnetic (AFM) orientations of Co ion's magnetic moments. Our results showed that the FM phase is lower in energy than the AFM one, by 3 meV (or ∼30 K; that is an order of magnitude smaller than the experimental value of T_C). The obtained magnetic moment value for Co ions in the ground state is 3 μ_B. Thus, the exchange interaction of magnetic ions is FM, but weak even for an impurity concentration larger than the ones in fabricated samples

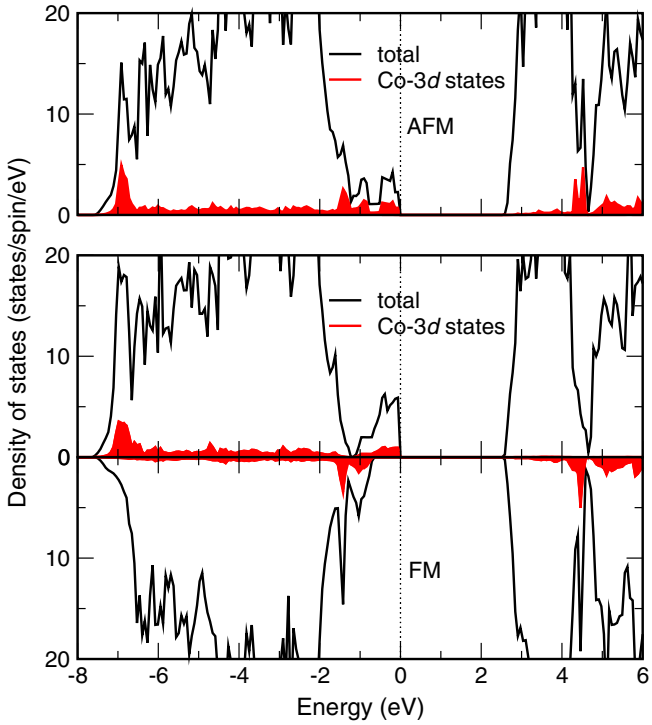

Figure 2. Total and partial densities of states obtained from the LSDA + U calculations for antiferromagnetic (AFM; top panel) and ferromagnetic (FM; bottom panel) configurations of Co ions in $Co_{1/8}Ti_{1-1/8}O_2$ model compound.

of Co-doped TiO_2 [6]. Therefore, the exchange interaction between the magnetic moments of impurities alone, without taking into account other states, cannot yield as high T_C as observed.

3. Titanium dioxide with oxygen vacancies

In order to explore the electronic structure and magnetic property changes caused by the localized states produced by oxygen vacancies, we first considered a supercell containing four formula units of TiO_2 with one oxygen atom replaced by an empty sphere; it corresponds to $TiO_{2-1/8}$ composition. The result of the LSDA + U calculation is shown in figure 1 (bottom panel). The electronic structure for an oxygen vacancy exhibits a narrow defect band, which is fully occupied. It is formed of mainly Ti d-states of the Ti ions near the vacancy, split off from the bottom of the conduction band and has a symmetry of s orbital centred on the vacancy site. The two electrons added to the system as a result of removing the O^{2-} ion occupy this band of s symmetry and result in a nonmagnetic ground state. To obtain a magnetic solution and, consequently, localized moment, this band should be partially filled. That corresponds to a so-called F^+-centre with one electron localized on an oxygen vacancy state.

To study a half-filled vacancy band (still without explicitly considering cobalt impurity), we added one hole per supercell. Physically such occupancy of the defect states could be realized if the system contains one Co^{2+} impurity per two oxygen vacancies or one Ti vacancy per four oxygen vacancies. In all our further calculations we added the number of holes which would provide half-filled bands formed of oxygen vacancies.

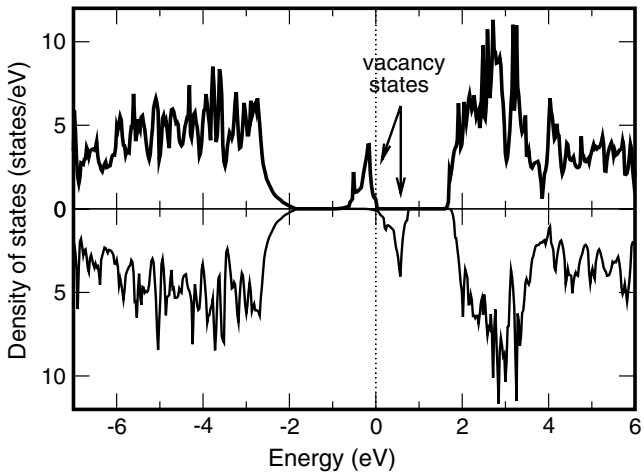

Figure 3. Total density of states for oxygen deficient $TiO_{2-1/8}$ model compound in the magnetic state. Fermi energy is zero.

The partial occupancy of the defect band results in a spin-polarized magnetic solution. The magnetic state has a lower total energy in comparison with the nonmagnetic one; thus, it is the ground state of the system with the magnetic moment value per supercell of 1 μ_B. In figure 3 the density of states for this magnetic solution is presented.

Considering our result one can assume that not only Co ions, but also vacancies yield sizeable magnetic signals in Co-doped TiO_2. A similar idea was proposed in a recent paper [24], where observed room-temperature ferromagnetism in ZnO was interpreted in terms of a spin-split donor impurity-band model, and F^+ centres, associated with oxygen vacancies, were considered as a possible source of magnetism. In principle, vacancies themselves without magnetic impurities could induce magnetization as was shown in the work of Monnier *et al* [25]. They observed high temperature ferromagnetism in normally pure CaB_6, fabricated under Ca-poor growth conditions. In these crystals the strong covalency of the B–B bonds makes the formation of B-vacancies more energetically preferable. Large values of magnetic moments could be obtained in the distorted lattices where vacancies are located nearby.

We have also investigated the exchange interaction between vacancies, considered FM and AFM configurations of vacancies moments. We dealt with a supercell containing eight formula units with two oxygen vacancies in a supercell; it corresponds again to $TiO_{2-1/8}$ composition. The results of the LSDA + U calculations showed that the AFM solution is lower in energy by 50 meV. This can be explained by the Hubbard model theory. It predicts that AFM solution is the ground state in the case of the half-filled band.

The next step is to study how the vacancy moment interacts with the Co one and how the presence of the vacancy influences the Co–Co interaction.

4. Cobalt-doped titanium dioxide with oxygen vacancies

In order to explore the influence of vacancy states on the magnetism of Co-doped TiO_2, we considered a supercell containing eight formula units with one Co impurity and one oxygen vacancy at three different possible distances from each other. The energy difference between FM and AFM configurations of Co and the vacancy was calculated for each case within the LSDA + U approach to estimate the strength of the exchange interaction between Co and

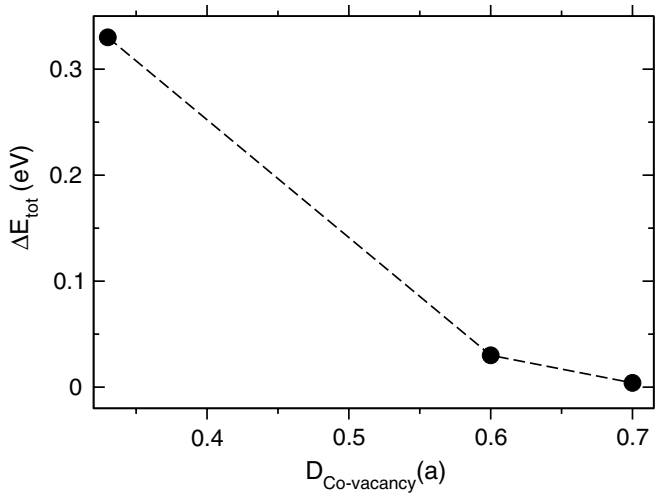

Figure 4. The energy difference between FM and AFM configurations of Co and vacancy moments as a function of distance between them for $Co_{1/8}Ti_{1-1/8}O_{2-1/8}$ model compound. Distance is given in the units of lattice constant $a = 5.92$ Å.

the vacancy magnetic moments. As in the previous section, the total number of electrons in the supercell was adjusted to produce divalent Co^{2+} ions and half-filled oxygen vacancy states (F^+-centres). That required adding one electron to the supercell because every vacancy adds two electrons to the system and two electrons are removed when a tetravalent Ti^{4+} ion is substituted by divalent Co^{2+}. That could be realized by the presence of an additional oxygen vacancy per Co–vacancy pair but without considering explicitly the corresponding localized states.

The results obtained are presented in figure 4. In all three cases, the AFM arrangement of Co and vacancy spins is lower in energy. The calculated moments of Co and vacancy are 3 μ_B and -1 μ_B, respectively. Thus, oxygen vacancy prefers to have the magnetic moment that is AFM ordered to Co moment. One can see (figure 4) that the strength of interaction between Co and the vacancy drops rapidly with the increase in the distance between them. For the nearest and the longest distances of 1.9 and 4.1 Å, the energy difference values are 330 and 40 meV, respectively. This energy interval corresponds to the temperature range from ∼3800 to 500 K. We assume that the presence of a strong exchange interaction between Co and vacancy moments might result in a strongly coupled system of Co and the magnetic moments of vacancies with a high ordering temperature.

To investigate vacancy influence on the strength of the exchange interaction between Co spins, we used the same supercell as in section 2, but with one oxygen ion removed from it. We chose the position of the oxygen vacancy to be at an equal distance of 3.58 Å from both Co ions. Again, the total number of electrons in the supercell was adjusted to produce divalent Co^{2+} ions and half-filled oxygen vacancy states (F^+-centres). In this case, that required adding three electrons to the supercell. (Similarly to the previous case, that could be realized by the presence of three additional oxygen vacancies per supercell but without explicitly considering the corresponding localized states.)

Total and partial densities of states for AFM and FM configurations of Co ions obtained from the LSDA + U calculations are shown in figure 5. One can see that vacancy induced states are situated around the Fermi level between occupied and unoccupied Co 3d states without overlapping them. This electronic structure rather agrees with the scheme proposed for Mn

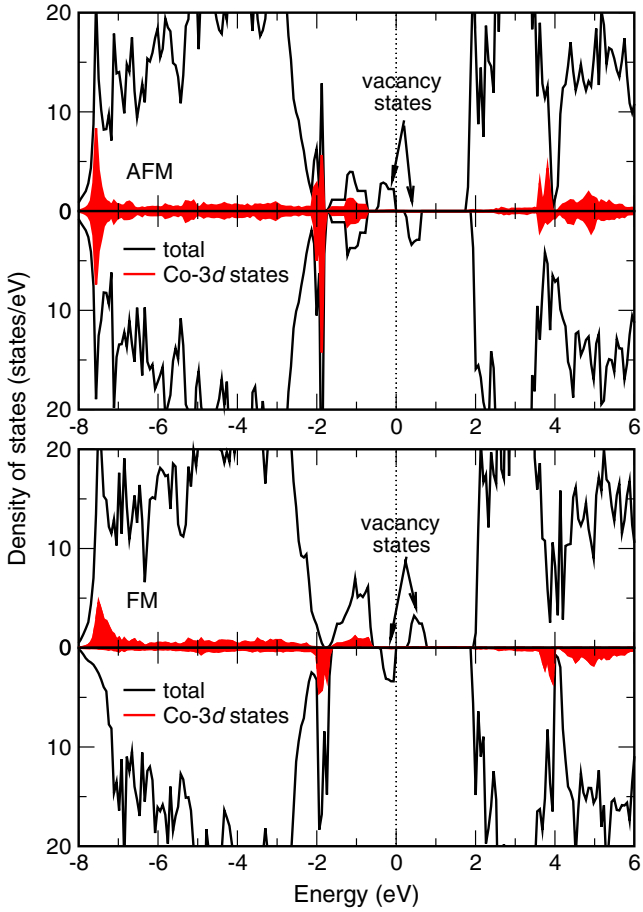

Figure 5. Total and partial densities of states for AFM (top panel) and FM (bottom panel) configurations of Co ions in $Co_{1/8}Ti_{1-1/8}O_{2-1/16}$ model compound obtained from the LSDA + U calculations. Zero of energy is at the Fermi energy.

impurity in a spin-split donor impurity-band model [24], where there is no overlap of vacancy band with 3d states. But in contrast to that, vacancy states are not in the middle of Co majority and minority states, but shifted closer to the occupied 3d states, although without overlapping, like in the scheme proposed for Ti in [24].

From the calculations, we found that the strength of magnetic ion interaction in the presence of a vacancy is three times stronger than that without a vacancy. The corresponding energy difference between AFM and FM configurations of Co ions is equal to 10 meV; FM orientation of Co magnetic moments is lower in energy. The obtained total cell magnetization is 5 μ_B. At that each Co accounts for 3 μ_B. The vacancy moment is equal to 1 μ_B and is AFM ordered with respect to the Co moments. The solution with FM order of moments is not stable. Again, the oxygen vacancy moment prefers to be AFM ordered to Co one like in the previous case of one Co and vacancy in the cell, which leads to in a FM coupling between Co ion moments.

The next step in the investigation of vacancy influence on Co spin interaction is to examine it when the defect state band is empty or full, and, hence, the vacancy is nonmagnetic. As the

Table 1. The list of supercells used in calculations: model of the calculation, type of magnetic ordering between Co ions, oxygen vacancies (Vac) or Co–vacancy, ΔE is the difference between FM and AFM configurations. In the third and fourth models the distance (D) between Co and the vacancy is given. The last two cases correspond to half-filled and empty/full-filled vacancy states.

Model	Type of ordering	ΔE (meV)
$Co_{1/8}Ti_{1-1/8}O_{2-1/8}$ (16 f.u., 2 Co)	Co–Co	3
$TiO_{2-1/8}$ (8 f.u., 2 Vac)	Vac–Vac	50
$Co_{1/8}Ti_{1-1/8}O_{2-1/8}$ (8 f.u., 1 Co, 1 Vac)	Co–Vac ($D = 1.9$ Å)	330
$Co_{1/8}Ti_{1-1/8}O_{2-1/8}$ (8 f.u., 1 Co, 1 Vac)	Co–Vac ($D = 4.1$ Å)	40
$Co_{1/8}Ti_{1-1/8}O_{2-1/8}$ (16 f.u., 2 Co, 1 Vac)	Co–Co (half-filled)	10
$Co_{1/8}Ti_{1-1/8}O_{2-1/8}$ (16 f.u., 2 Co, 1 Vac)	Co–Co (empty/full-filled)	3

vacancy states are situated between Co majority and minority d-states (figure 5), the addition of an electron or a hole makes the band full or empty, respectively, but does not change the Co valence. The energy difference between the FM and AFM configurations of the Co ions appears to be about 3 meV in the case of both empty and full defect state bands, like in the supercell without vacancy. Thus, the presence of an oxygen vacancy enhances the Co ion's interaction only when the vacancy is magnetic.

5. Conclusion

In summary, using the LSDA+U approach we have investigated the role of magnetic impurities and oxygen vacancies in the formation of ferromagnetism with high T_C in Co-doped TiO_2. We found that the exchange interaction of magnetic Co ions is ferromagnetic, but very weak due to the large average impurity–impurity distance. However, it becomes three times stronger when there is a magnetic vacancy present. The obtained magnetic moments are 3 μ_B and 1 μ_B for Co and the vacancy, respectively. We also found that the interaction between Co and vacancy moments is surprisingly very strong even for the longest distance of 4.1 Å in the supercell. In this case, the energy difference between FM and AFM configurations of Co and vacancy moments is 40 meV, which corresponds to ∼500 K. Our results lead us to think that the observed magnetic signal cannot be attributed to Co ions alone: the moments of vacancies should be taken into consideration too. It seems that the strong interaction between Co and vacancy moments is a key moment for the explanation of high T_C in Co-doped TiO_2.

Acknowledgments

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