PHYSICAL REVIEW B **69**, 125219 (2004)

Electronic structure and optical properties of the Co-doped anatase TiO_2 studied from first principles

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(Received 3 August 2003; revised manuscript received 1 December 2003; published 30 March 2004)

The Co-doped anatase TiO_2, a recently discovered room-temperature ferromagnetic insulator, has been studied by the first-principles calculations in the pseudopotential plane-wave formalism within the local-spin-density approximation, supplemented by the full-potential linear augmented plane-wave method. Emphasis is placed on the dependence of its electronic structures and linear optical properties on the Co-doping concentration and oxygen vacancy in the system in order to pursue the origin of its ferromagnetism. In the case of substitutional doping of Co for Ti, our calculated results are well consistent with the experimental data, showing that Co is in its low spin state. Also, it is shown that the oxygen vacancy enhances the ferromagnetism and has larger effect on both the electronic structure and optical properties than the Co-doping concentration only.

DOI: 10.1103/PhysRevB.69.125219 PACS number(s): 75.50.Pp, 71.20.Nr, 78.20.Bh

I. INTRODUCTION

The discovery of the ferromagnetic semiconductor has stimulated a great deal of interests in the origin of its ferromagnetism because of its potential applications in the spintronics, a rapidly developing research area, in which the electron spin plays an important role in addition to the usual charge degree of freedom. In fact, the diluted ferromagnetic semiconductors (DMS's) based on II-VI compound semiconductor had been studied for over 20 years.[1] The transition-metal magnetic impurities are often used as spin injector to cause the giant magnetoresistance and magneto-optical effect. But usually, it is the *n*-type carrier doping with concentration of 10^{19} cm^{-3} in maximum and the *p*-type doping is difficult. This drawback results in a lower ferromagnetic Curie temperature T_c in the order of ~ 1 K, which is well explained by the carrier-induced mechanism.[2] On the other hand, ferromagnetism with Curie temperature as high as 110 K was discovered[3] in III-V compound based DMS's, such as GaAs doped with Mn ion. The strong *p-d* exchange interaction intermediated by mobile holes is thought of as the origin of ferromagnetism with so higher Curie temperature.[4] However, both of them are still far from the practical use at room temperature. Therefore, a lot of effort has been made continuously in the recent years in order to get higher and higher T_c DMS's. Motivated by this, the transition-metal oxide based DMS's have been buoyed up as a candidate of the room-temperature DMS's.

Excitedly, Matsumoto *et al.*[5] reported that Co-doped anatase TiO_2 ($Ti_{1-x}Co_xO_{2-\delta}$) can keep ferromagnetic order up to 400 K with magnetic moment about 0.32 μ_B/Co, which was explained by the carrier-induced ferromagnetism with the exchange interaction mediated by electrons not holes. Chamber *et al.*[6,7] had reproduced the ferromagnetic $Ti_{1-x}Co_xO_{2-\delta}$, but found the magnetic moment on Co is as high as 1.25 μ_B. They considered that the ferromagnetism strongly depends on the oxygen deficiency. Because recent theoretical[8] and experimental[9] studies show that oxygen vacancies resulted from the substitution of Co (II) for Ti (IV) do not contribute to carriers, Kim *et al.*[10] and Shinde and Ogale[11] paid more attention to the role of Co in the origin of the ferromagnetism. They thought that some amount of Co clusters induce the ferromagnetism, but their thermal treatment is quite questionable, and in fact, the measurement of magnetic circular dichroism spectrum done by Fukumura "rules out the apparent precipitation of Co metal as a source of ferromagnetic signal."[12] More recently, Ogale *et al.*[13] found that the thin films of $Sn_{1-x}Co_xO_{2-\delta}$ ($x<0.3$) not only exhibit ferromagnetism with a Curie temperature close to 650 K, but also a giant magnetic moment of (7.5 ± 0.5) μ_B/Co, which is much larger than the value for small Co clusters (~ 2.1 μ_B/Co) and offers another evidence to disfavor the Co cluster contribution to the ferromagnetism in the transparent Co-doped TiO_2 and SnO_2. Simpson *et al.*[14] studied the optical conductivity of the $Ti_{1-x}Co_xO_{2-\delta}$, and concluded that the Co atom is not substitutional but interstitial or forms Co-Ti-O complex based upon the absence of in-band-gap absorption and the blue shift of absorption edge with increasing *x*. On the other hand, the first-principles calculation done by Sullivan[8] supported this idea, and showed that "*n*-type behavior in Co-doped TiO_2 requires a substantial amount of Co to be in the interstitial form, and that this can only happen under O-poor growth conditions." So, at the present time, the origin of the ferromagnetism and the high Curie temperature of $Ti_{1-x}Co_xO_{2-\delta}$ are still controversial, and more experimental and theoretical studies are needed.

In this paper, we have used CASTEP (Ref. 15) to study the electronic structures and optical properties of $Ti_{1-x}Co_xO_{2-\delta}$ in four different configurations, which are ($x=0.0417,\delta=0$), ($x=0.062,\delta=0$), and ($x=0.0625,\delta=0.0625$) with oxygen vacancy near Co atom and Ti atom, respectively. Our results show that variation of *x* from 0.0417 to 0.0625 causes little difference of the electronic structures and optical properties, but the oxygen vacancy changes them greatly. In the local-spin-density approximation (LSDA), the magnetic moment about 0.68 μ_B per Co atom has been obtained in the first and second cases. The oxygen vacancy near Co atom in the third case causes increase of the magnetic moment on Co to about $-0.90\ \mu_B$, while in the fourth case the oxygen vacancy near Ti changes this value to $-0.38\ \mu_B$. The relative positions of the optical conductivity peaks in the first three configurations are quite comparable with the experimental results,[14] while in the fourth one they are totally different. All these results support the idea of Chamber *et al.*[6,7] that the ferromagnetism strongly depends on the oxygen deficiency. Moreover, total energy of the system in the third case is lower than that in the fourth one by about 0.33 eV per anatase cell, indicating that the oxygen vacancy prefers to stay near Co than near Ti.[9]

II. CALCULATION METHOD

The software package CASTEP (Ref. 15) has been used in our calculations, which is based on a total-energy pseudopotential plane-wave method within the LSDA. In the calculation, the Perdew and Zunger's form of the exchange-correlation energy has been used.[16,17] The ion-electron interaction is modeled by ultrasoft local pseudopotentials in the Vanderbilt form.[18] The maximum plane-wave cutoff energy is taken as 280 eV. In the spin optimization, the initial spin configuration is taken as one net spin on Co atoms, and the initial crystal structures of the $\mathrm{Ti}_{1-x}\mathrm{Co}_x\mathrm{O}_{2-\delta}$ with $x=0.0625$ and $x=0.0417$ are taken as a $(2\times2\times1)$ and a $(2\times3\times1)$ supercell,[19–22] respectively, in which only one apical Ti is replaced by Co. In the case of $x=0.0625$, one oxygen atom can be removed from the octahedra containing Co or that containing Ti, forming two different configurations called as the third and fourth cases, respectively. In every case, the geometrical optimization is always made and convergence is assumed when the forces on atoms are less than 50 meV/Å, based upon which the electronic structures are then calculated. Finally, within the electric-dipole approximation, the imaginary parts of the dielectric functions can be calculated by the following formula:

$$\varepsilon_2(\omega)=\frac{8\pi^2e^2}{\omega^2m^2V}\sum_{c,v}\sum_{k}|\langle c,k|\hat{\mathbf{e}}\cdot\mathbf{p}|v,k\rangle|^2 \times\delta[E_c(k)-E_v(k)-\hbar\omega],$$

where c and v represent the conduction and valence bands, respectively. $|n,k\rangle$ is the eigenstate obtained from CASTEP (Ref. 15) calculation. $\mathbf{p}$ is the momentum operator and $\hat{\mathbf{e}}$ is the external field vector. ω is the frequency of incident photons. We use a $4\times4\times4$ grid of k points to make an integration over the Brillouin Zone. Using Kramers-Krönig transformation, we can get the real part ε_1 of the dielectric function and then according to the formula of $\sigma=\sigma_1+i\sigma_2=-i(\omega/4\pi)(\varepsilon_1+i\varepsilon_2-1)$, the optical conductivity is finally obtained.

III. RESULTS AND DISCUSSION

The CASTEP optimized geometrical structures together with the spin densities in (010) plane of $\mathrm{Ti}_{1-x}\mathrm{Co}_x\mathrm{O}_{2-\delta}$ for different x and δ values are shown in Fig. 1, in which the number beside the atom represents the magnetic moment obtained by Mulliken analysis, and its sign indicates the positive or negative moment. It can be seen from Fig. 1 that the geometrical structure of the system is changed very little by the doped Co atom, but one oxygen atom vacancy causes a remarkable distortion of the original octahedral structure, leading to changes of the electronic structures. For example, comparison of Figs. 1(a) and 1(b) indicates that more Co concentrations cause the spin density to be more connective in space even without oxygen vacancy. On the other hand, however, comparison of Figs. 1(b) and 1(c) shows that at the same Co concentration, the geometrical structure distortion induced by the oxygen vacancy will make the spin density further heavily connected in space along the direction of Co-oxygen vacancy, indicating clearly that the oxygen vacancy plays a role of enhancing the ferromagnetism. The emergency of spin density on the Ti atom should be another noticeable indication of the heavier connectivity of spin density in space than that without oxygen vacancy at the same Co concentration. In Figs. 1(d) and 1(e), although the oxygen vacancy is far away from the Co atom, it still has larger effect on the physical properties of the system, which is contrary to the result of Park *et al.*[19] Some oxygen atoms are pushed outside of the plane (010) in Fig. 1(d), and spin density appears on Ti, making the spin density to be connective in space too. Furthermore, we have also made an antiferromagnetic (AFM) first-principles calculation in the third case (i.e., with oxygen vacancy near Co atom), from which it is found that independent of the initial spin configurations, the CASTEP calculation performed in a doubly enlarged supercell[20] always converges to the FM ground state with an averaged magnetic moment of about $-0.9\mu_B$ on each Co atom, while for such a supercell in the second case, the AFM ground state is always obtained,[20] clarifying more clearly the importance of the oxygen vacancy for FM coupling. More careful analyses show that the electrons on Co and Ti are *d*-type-like, and those on O atoms are *p*-type-like, and from Mulliken analysis, it is known that in Fig. 1(c) the spin on Ti atom nearest to Co is antiparallel to that on Co, while the spin on the next nearest Ti is parallel to that of Co. In Fig. 1(d), however, those spins on Ti and Co are all in parallel. So the spin on Ti atom should not be ignored when we try to pursue the origin of the ferromagnetism in the Co-doped TiO_2. Comparison of Figs. 1(c) and 1(e) tells us that without Co but only oxygen vacancy would not cause ferromagnetism.

Now, we turn to the density of states (DOS) shown in Fig. 2. Due to the well-known shortcomings of the LSDA, our electronic structure shows half metallic $\mathrm{Ti}_{1-x}\mathrm{Co}_x\mathrm{O}_{2-\delta}$. It is clearly seen from Figs. 2(a) and 2(b) that when x changes from 0.0417 to 0.0625, the DOS changes very little, not only the total DOS but also all the partial DOS's for each kind of atoms. Compared with the LMTO results obtained by Park *et al.*,[19] it is known that the main difference lies in the energy

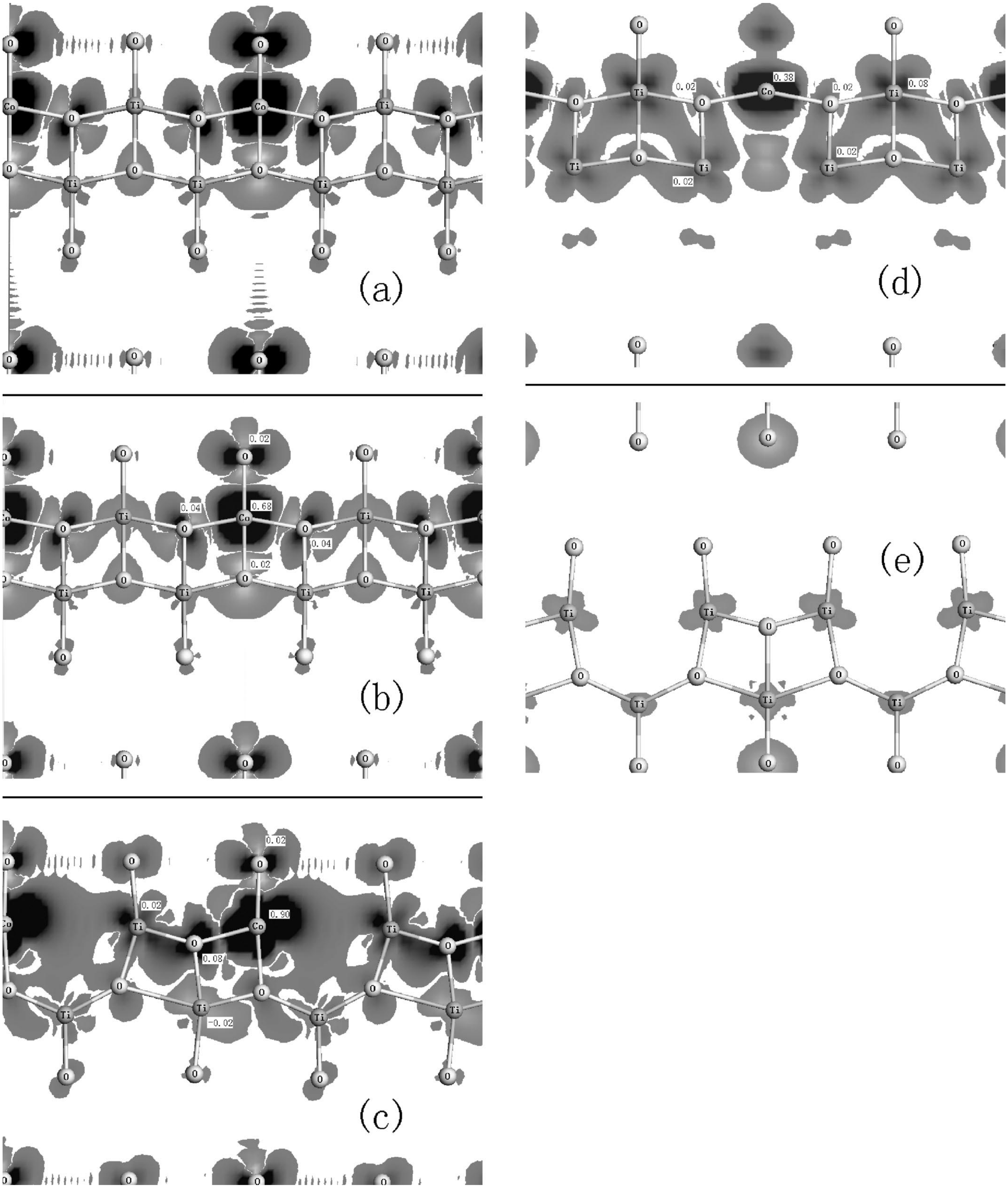

FIG. 1. The optimized structure and spin density of $Ti_{1-x}Co_xO_{2-\delta}$ in the plane (010) when (a) $x=0.0417$, $\delta=0$; (b) $x=0.0625$, $\delta=0$; (c) $x=0.0625$, $\delta=0.0625$ with oxygen vacancy near Co; (d) $x=0.0625$, $\delta=0.0625$ with oxygen vacancy near Ti, which does not lie in the plane (010); and (e) $x=0.0625$, $\delta=0.0625$ with oxygen vacancy near Ti in the plane. The number beside the atom represents its magnetic moment obtained by Mulliken analysis, and its sign indicates the positive or negative moment.

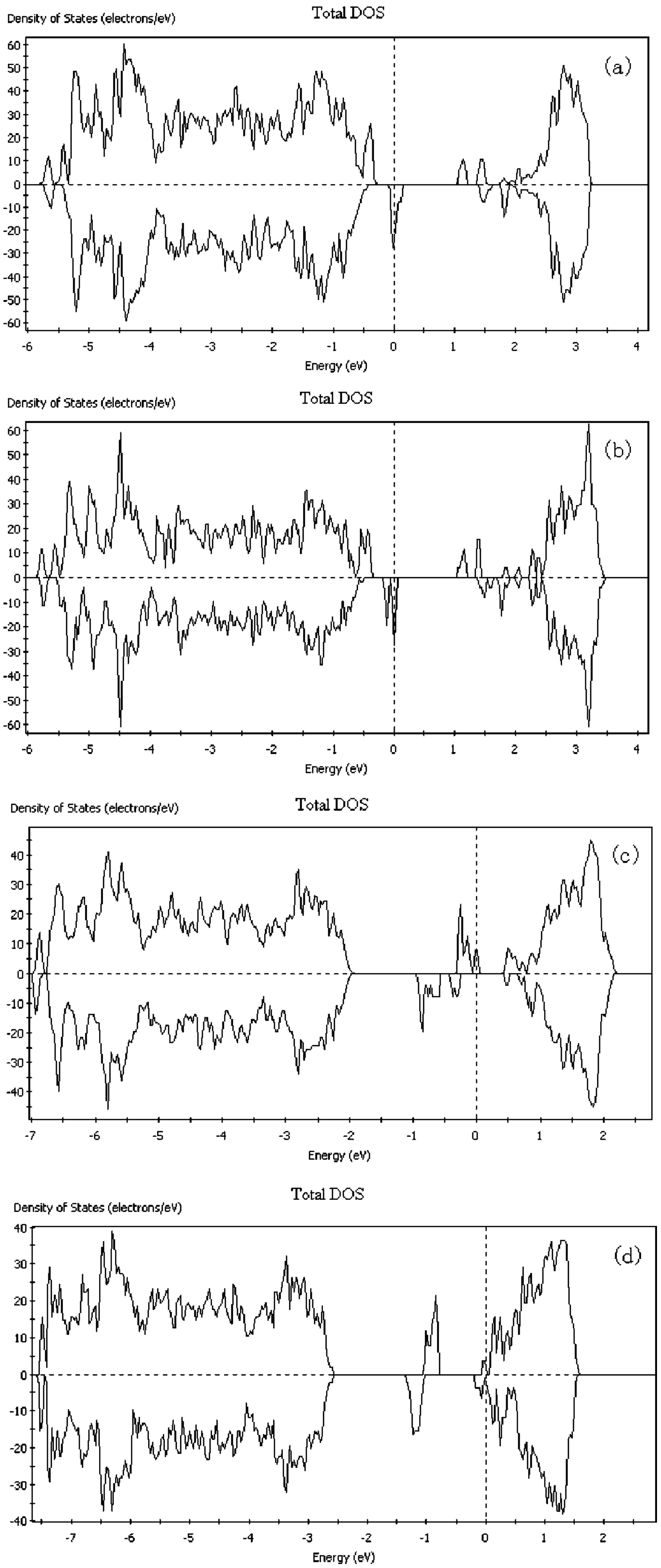

FIG. 2. The spin-polarized DOS of $Ti_{1-x}Co_xO_{2-\delta}$ when (a) $x=0.0417$, $\delta=0$; (b) $x=0.0625$, $\delta=0$; (c) $x=0.0625$, $\delta=0.0625$ with oxygen vacancy near Co; and (d) $x=0.0625$, $\delta=0.0625$ with oxygen vacancy near Ti. The positive DOS means that of spin up while the negative is for spin down.

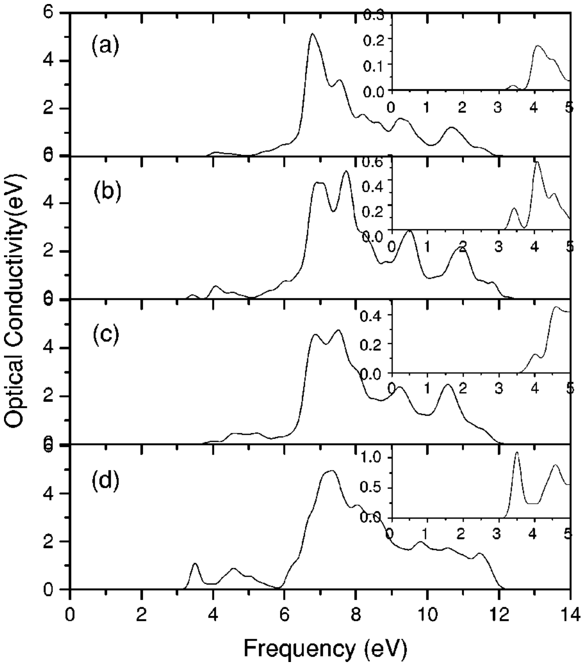

FIG. 3. The optical conductivity of $Ti_{1-x}Co_xO_{2-\delta}$ when (a) $x=0.0417$, $\delta=0$; (b) $x=0.0625$, $\delta=0$; (c) $x=0.0625$, $\delta=0.0625$ with oxygen vacancy near Co; and (d) $x=0.0625$, $\delta=0.0625$ with oxygen vacancy near Ti. Each inset is the magnified spectrum in the energy range between 0 and 5 eV.

region above 2 eV. On the other hand, the oxygen vacancy changes the DOS more, especially those around the Fermi level. Figure 2(c) shows that the Fermi level shifts upward by about 1.2 eV compared to Fig. 2(b) and the major spin becomes spin up. The oxygen vacancy near Co also makes the first gap above Fermi energy narrower, from about 1 eV to 0.5 eV, and thus will make the thermal excitation easier and generate more charge carriers. As shown in Fig. 2(d), the oxygen vacancy near Ti has bigger effects on the total DOS than near Co shown in Fig. 2(c), shifting the Fermi level further up by about 0.75 eV, and causing much less DOS on the Fermi level. Most importantly, in this case, the system is no longer a half metal but a metal.

It is a powerful and natural method to investigate the electronic structure of material by its optical response. The experimental absorption edge of the Co-doped anatase TiO_2 is the same as that of the pure anatase TiO_2, i.e., at about 3.2 eV.[14] So, in our calculation, we have used the scissor approximation to fit the calculated absorption edge to the experimental value, and shown in Fig. 3 thus obtained optical conductivities for all four cases. For clarity, the spectrum in the range of 0–5 eV is magnified and shown in the inset. It is seen from Figs. 3(a) and 3(b) that in the energy range of 0–6 eV, the peak values of $x=0.0417$ are smaller than those of $x=0.0625$, which seems to be contrary to the experimental data in Ref. 14 because there the corresponding peak values decrease with x increasing. But, the peak positions in both cases match well, indicating that different Co concentrations do not change the peak positions. Again, we focus our attention to the oxygen-vacancy effects on the optical property of $Ti_{1-x}Co_xO_{2-\delta}$. It is seen from Fig. 3(c) that the absorption

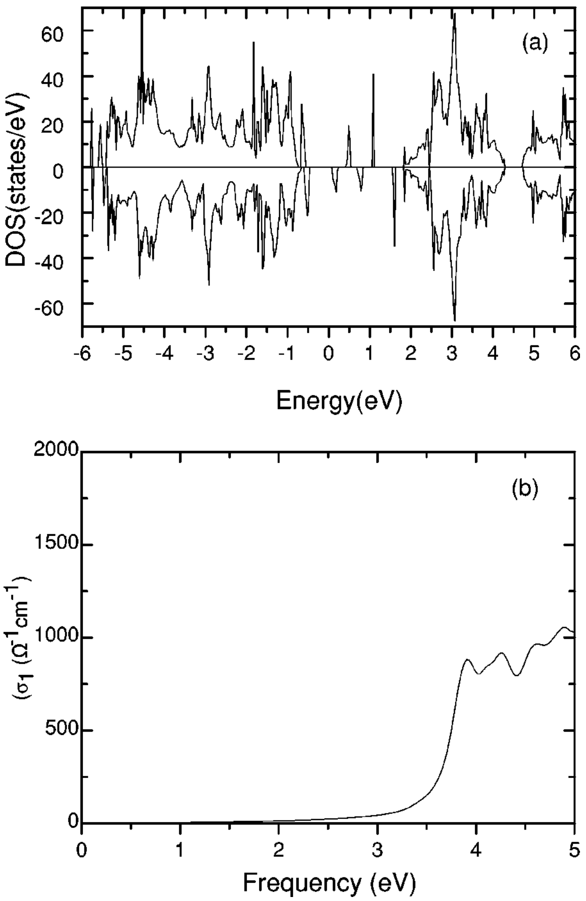

FIG. 4. The DOS (a) and optical conductivity(b) of $Ti_{1-x}Co_xO_{2-\delta}$ for $x=0.0625$, $\delta=0$, calculated by LSDA$+U$ in the FP-LAPW formalism with $U=3.0$ eV.

edge shifts to a higher energy at about 3.6 eV and its first peak appears at about 4.0 eV, which is not shown in the experiment because its measurement range is limited to 3.7 eV and further experimental data are needed to confirm this point. While above 6.0 eV, the peak positions, even their values, are the same as those of the second case with no oxygen vacancy, which can be explained by the difference between two DOS's in Figss. 2(b) and 2(c). As shown in Fig. 2(d), the oxygen vacancy near Ti has led to completely new DOS's around the Fermi level, giving thus a rather different optical responses, compared with other three cases. Now, the first peak lies at about 3.5 eV, which is not seen in the experiment. So, taking the total energy into account, we consider that in the real materials, the oxygen vacancy rarely occupies the site near Ti, but prefers near Co.

In order to overcome the shortcomings of the simple LSDA calculations and also compare our calculated results more reasonably with the experiments, we have further made the LSDA$+U$ calculations in the case of $x=0.0625$, $\delta=0.0$ in the full-potential linear augmented plane-wave[23] (FP-LAPW) formalism with $U=3.0$ eV (Ref. 19) by using the same CASTEP optimized structure.[20] Obtained DOS in this case is shown in Fig. 4(a). Comparing it with Fig. 2(b) obtained by CASTEP, we can see that there is no big change of the DOS for the most of the valence and conduction bands, except for appearance of an energy gap ≈ 0.8 eV around the Fermi level, indicating that the system becomes a semiconductor and is in good agreement with the experimental data for the case of $x=0.0625$, $\delta=0.0$. In addition, we have also calculated its optical conductivity by the LSDA$+U$ in the FP-LAPW formalism with the same $U=3.0$ eV. Due to well-known reason, the energy gap of about 0.8 eV obtained by the FP-LAPW$+U$ method is still much less than the experimental value of ~ 3.2 eV. Therefore, the same scissor approximation is used to fit the absorption edge. The obtained result is shown in Fig. 4(b), which, compared with Fig. 3(b), seems to match better the observed data, not only the peak positions but also their heights, indicating that our Co-substitutional model for the $Ti_{1-x}Co_xO_{2-\delta}$ is rather reasonable and the on-site Coulomb interaction of the Co atom plays an important role in the physical properties of the system, and in general should be included.

IV. CONCLUSION

In summary, assuming the substitutional doping of Co for Ti, we have studied the effects of different Co-doping concentrations and oxygen vacancies on the electronic structures and optical properties of the $Ti_{1-x}Co_xO_{2-\delta}$ by the first-principles calculations. Our obtained results show that the doped Co concentrations from 0.0417 to 0.0625 have only a little effect on them, but the oxygen vacancy and its distribution in the system have much larger influences, especially on the ferromagnetism and optical properties of the Co-doped anatase TiO_2.

ACKNOWLEDGMENTS

The authors acknowledge support to this work from a Grant for State Key Program of China through Grant No. 1998061407 and National Science Foundation under Grant No. 90103038. J.D. acknowledges greatly support from a Grant under the Grant No. 14GS0204 in the IMR of Tohoku university in Sendai of Japan and valuable discussions about the $Ti_{1-x}Co_xO_{2-\delta}$ with Dr. T. Fukumura in the IMR. Our calculations have been done on the SGI origin 2000 and 3800 Computers.

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