Structural, electronic, and magnetic properties of a ferromagnetic semiconductor: Co-doped TiO₂ rutile

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The local environment around magnetic impurity atoms was reported to be unchanged in a structural phase transition of nanocrystalline Co-doped ferromagnetic TiO_2 . Our *ab initio* density functional theory investigations show that the substitutional Co ions incorporated into TiO_2 rutile tend to cluster, and then the neighboring interstitial sites become energetically favorable for Co to reside. This suggests that a Co-doped rutile containing only substitutional Co may not be an appropriate reference bulk system in determining the local environment of Co in polycrystalline (Ti,Co)O₂ rutile. We also find that the interstitial Co is in the low spin state and destroys the spin polarization of the surrounding substitutional Co, and hence reduces the average magnetic moment of impurity atoms.

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I. INTRODUCTION

Spintronics has emerged expeditiously as an interesting technology where both charge and spin are harnessed for new functionalities in devices combining standard microelectronics with spin-dependent effect.^{1,2,3} For their practical spintronic applications, a ferromagnetic semiconductor is required to be not only easily integrable but also to have a high Curie temperature. The development of new materials has grown rapidly. Room-temperature ferromagnetism has been observed, for instance, in Mn-doped ternary compounds such as CdGeP₂,⁴ ZnSnAs₂,⁵ and ZnGeP₂.⁶ A recent discovery of room-temperature ferromagnetism in Co-doped TiO₂ anatase by Matsumoto et al.⁷ using a combinatorial molecular beam epitaxy technique, has motivated intensive studies on the structural and physical properties of this material.^{8,9,10,11,12} Transparent to visible light, this material is expected to be of particular importance in spin-based optoelectronic applications such as spin-light-emission-diode and optical switches operating at a terahertz frequency.³

It is interesting to note that Matsumoto *et al.* observed a magnetic structure only in $(Ti,Co)O_2$ anatase but not in the rutile phase,¹³ seemingly suggesting that the magnetization of the impurity atoms depends sensitively on the local environment surrounding them. More recently, however, Park *et al.* have successfully grown ferromagnetic $(Ti,Co)O_2$ rutile films by sputtering.¹⁴ The Curie temperature was estimated to be above 400 K for a Co content of 12%. Since the rutile phase is thermodynamically more stable than the anatase phase, it may have a higher potential for technical applications. The dissimilar behaviors of films grown by different methods indicate that the local environment of Co could have a drastic effect on the magnetic structure of this material. Furthermore, by annealing the $(Ti,Co)O_2$ samples pre-

pared by the sol-gel method at different temperatures, Soo *et al.* found that the local structure around Co could remain virtually anataselike while the nanomaterials underwent an anatase-to-rutile phase transition.¹⁵ This discovery is rather unique, and certainly deserves more detailed investigation in order to gain a microscopic understanding of the magnetism displayed by this intriguing material.

Here we point out that in extracting the information of the local structure of Co through the x-ray absorption fine structure method, Soo et al. employed a reference bulk system assuming all Co ions substitute for the Ti sites in rutile TiO_2 .¹⁵ In a recent work,¹¹ we showed by *ab initio* density functional theory study that Co could also occupy interstitial sites in anatase TiO_2 . The question that arises is this: Is it also the case for Co-doped rutile TiO₂? To answer this question, we have performed a computational investigation on the structural, electronic, and magnetic properties of Co-doped TiO₂ rutile. We show that substitutional Co ions tend to cluster, but this has no remarkable effect on the magnetization of Co. We also find that an interstitial site will become energetically favorable for a Co atom (in reference to bulk Co) when two of its neighboring substitutional sites are occupied by Co. The interstitial Co is in the low spin state $(0.94\mu_{\rm B})$, but it exerts a strong detrimental effect on the magnetization of its neighboring Co (0.76 $\mu_B \rightarrow -0.03 \mu_B$) and therefore reduces the magnetic moment Co in this magnetic semiconductor. In the following, we give a brief outline of our theoretical procedure, and a discussion of the results based on bonding characteristics and its relevance to our understanding of the magnetism in this Co-doped oxide.

II. CALCULATION

The calculations were done using a spin-polarized version of the Vienna *ab initio* Simulation Package.¹⁶ Fully nonlocal



FIG. 1. Unit cells of non-doped [panel (a)] and Co-doped TiO_2 rutile [panel (b)]. Large and small circles represent O and Ti (Co), respectively.

Vanderbilt-type ultrasoft pseudopotentials¹⁷ were used to represent the electron-ion interaction. Exchange correlation interactions were described by the Perdew-Wang 1991 generalized gradient approximation (GGA).¹⁸ Wave functions and augmentation charges were expanded in terms of plane waves with energy cutoffs of 396 and 700 eV, respectively. For each system, the geometry was relaxed until the atomic forces were smaller than 0.03 eV/Å.

The six-atom rutile unit cell of TiO_2 [see Fig. 1(a)] is characterized by the two lattice constants a and c and the internal parameter u. The positions of Ti are (0, 0, 0) and (1/2, 1/2, 1/2), and those of O are (+/-u, +/-u, 0) and (+/-u/2,-/+u/2,1/2). The optimized a, c, and u are, respectively, 4.661 Å, 2.973 Å, and 0.638, in good agreement with experiment¹⁹ and previous pseudopotential GGA calculations.²⁰ For Co-doped cases, we mainly dealt with a supercell containing 16 primitive unit cells $[2a \times 2a \times 2c]$, see Fig. 1(b)], with one or two Ti atoms (site B1, or, sites B1 and B2) replaced by Co and with/without an interstitial Co (site A). Based on our knowledge of anatase $(Ti,Co)O_2$ that the volume contraction and expansion associated with substitutional and interstitial Co have only a negligible effect on the formation heat of $(Ti,Co)O_2$,¹¹ we fixed a and c at the calculated bulk TiO₂ values and optimized only internal freedoms upon Co doping.

III. RESULTS AND DISCUSSION

Whether Co atoms cluster or not depends not only on the formation energies for different distributions, but also on the microscopic diffusion mechanisms. The determination of the latter, however, involves an exhaustive investigation of the energetics of Co-Co complexes of various configurations, which is not affordable in the present study. Instead, we want

TABLE I. Calculated spin magnetic moment (μ_B) in the atomic sphere of Co (radius=1.10 Å) and that for a whole unit cell. Co(B1), Co(B2), and Co(A) denote Co ions occupying sites B1, B2, and A [see Fig. 1(b)].

Unit cell	Co(B1)	Co(B2)	Co(A)	Total
Ti ₁₅ Co ₁ O ₃₂	0.73	-	-	1.00
Ti ₁₄ Co ₂ O ₃₂	0.77	0.75	-	2.00
Ti ₁₄ Co ₃ O ₃₂	-0.03	-0.03	0.94	1.00

to see here whether Co atoms *tend* to cluster or not. Following the recent first-principles works on Mn-doped CdGeP₂,²¹ boron-²² and arsenic-doped silicon,²³ we have evaluated the pairing energy as the total energy difference between a Co-Co pair and well separated Co atoms in the host.

We first minimized the total energy of the cell Ti₇CoO₁₆ (Co content: 12.5%). Then we doubled this cell and brought the two Co^{S} together to form $Ti_{14}Co^{S}_{B1}Co^{S}_{B2}O_{32}$ ($2a \times 2a$ $\times 2c$). The latter configuration is found to be more stable by 0.31 eV/Co, indicating that Co clustering is very likely to occur at this concentration. The calculated formation energy of an interstitial Co (Co^I) as a neutral defect in reference to bulk Co, $E(Ti_{16}Co_A^IO_{32})-E(Ti_{16}O_{32})-E(Co)$, is +1.75 eV, implying that a sole Co^I is highly unstable in rutile TiO2. This can be understood in the bond-orderbond-strength picture. Ti:O+Co:O is much weaker than O:Ti:O, as is evident from a comparison of the formation heats of TiO_2 , TiO, and CoO.²⁴ Nonetheless, with the pres-ence of $\text{Co}_{\text{B1}}^{\text{S}}$, the formation energy of Co^{I} , i.e., $E(\text{Ti}_{15}\text{Co}_{\text{B1}}^{\text{S}}\text{Co}_{\text{A}}^{\text{I}}\text{O}_{32})$ - $E(\text{Ti}_{15}\text{Co}_{\text{B1}}^{\text{S}}\text{O}_{32})$ -E(Co), drops to +0.47 eV. According to our calculations, the formation heat of CoO_2 in a hypothetical rutile TiO₂ structure is -3.46 eV, slightly larger than twice that of CoO (-1.59 eV). This means that Co:O+Co:O is only slightly less stable than O:Co:O, thus Co^I becomes much less unstable. Further calculations show that when both B1 and B2 sites are occupied by Co upon clustering, site A becomes favorable for Co¹ with a formation energy of -0.72 eV. Once again, this can be explained by the formation heat of Co_3O_4 (-9.57 eV) greater than twice that of CoO_2 (-3.46 eV). Our calculations thus suggest a $2Co^{S}+Co^{I}$ local structure in Co-doped TiO₂ rutile. It should be noted that the formation of more complicated (Co^{S}, Co^{I}) combinations is also possible depending on the growth condition, but the formation probability should be lower than that of $2 \text{Co}^{\text{S}} + \text{Co}^{\text{I}}$.

In order to examine the effect of clustering on magnetism, we performed calculations on both intracell ferromagnetic (FM) and intracell antiferromagnetic (AFM) alignments of the Co pair in a Ti₁₄Co^SCo^SO₃₂ unit cell (for simplicity, we denote this cell as Ti₁₄Co₂O₃₂ in the following) while keeping the intercell coupling ferromagnetic. When the two Co atoms form a pair, occupying B1 and B2 sites, the AFM phase is found to be unstable and it switches to FM during self-consistency iterations. When they are far apart by 7.23 Å with one at (0, 0, 0) and the other at (*a*,*a*,*c*), the AFM phase is higher in total energy by 0.26 eV/Co than the FM phase. In the case of $2Co^{S}+Co^{I}$, we checked all three possible intra-



FIG. 2. Total density of states for nondoped and various cases of Co-doped TiO_2 rutile. Dotted vertical lines denote the Fermi energy.

cell spin alignments of the three Co ions. All of them converge to the same final state, with both Co^I and Co^S in the low spin state. The calculated total spin magnetic moment in a unit cell of $Ti_{15}Co_1O_{32}$, $Ti_{14}Co_2O_{32}$, and $Ti_{14}Co_3O_{32}$, and that in the atomic sphere of Co (radius 1.10 Å), are listed in Table I. It is seen that in all three cases, Co ions are in the low spin state, regardless of their oxidation states. The spin moment of Co^S does not change much upon clustering. Co^I, on the other hand, behaves rather differently. When coupled with Co^S, Co^I kills the spin moments of Co^S almost entirely.



As a result, the average spin magnetic moment of Co is reduced to 0.29 $\mu_{\rm B}$, less than a half of the non-Co^I value.

Figure 2 displays the calculated density of states for nondoped and various cases of Co-doped rutile. As in anatase,^{9,11} the Co states are mainly located in the energy-gap region and the O and Ti states are not much affected by Co doping. It is worth noting that with the GGA, while the anatase Ti₁₅Co₁O₃₂ and Ti₁₄Co₂O₃₂ miss being insulators, the Fermi energies of their rutile counterparts overpass the valence bands and fall into the energy gaps. The presence of Co^I does not change the insulating electronic structure of this material, though sole Co^I ions would turn the material into a metallic system (density of states not shown). This is another case where carriers are not necessary in order to generate roomtemperature ferromagnetic coupling in a semiconductor.⁶ In the absence of carriers, the spin interaction between dilute Co ions at low temperature can only be superexchange.²⁵ Superexchange interactions between local spins at cation sites mediated by diamagnetic anions in insulators such as MnO leads to antiferromagnetic coupling;²⁶ but those mediated by sp-d hybridization²⁷ in the II-VI diluted magnetic semiconductors can also lead to ferromagnetic coupling depending on the filling of ionic d shells of the incorporated magnetic transition metals.²⁸ Very recently, theory predicted²⁸ and experiment evidenced²⁹ ferromagnetic superexchange in Cr-based II-VI diluted magnetic semiconductors. However, as in the case of Mn-doped ZnGeP₂ (Ref. 6) and Co-doped TiO_2 anatase,⁷ the mechanism of the *room*temperature ferromagnetic superexchange in Co-doped TiO₂ rutile is still unclear.

In Fig. 3, we compare the 3*d* density of states (DOS) of Co in rutile with those of Co in other Co oxides with different oxidation states such as CoO_2 (+4) and Co_3O_4 (+3 and +2). CoO_2 , the end member of LiCoO2, has recently been isolated.³⁰ It seems to be of CdCl₂ type with a monoclinic distortion, but positions of O remain to be determined. In this regard, we believe that a study of a hypothetical CoO_2 in TiO2 rutile structure is meaningful in illustrating the electronic structure of Co^{4+} . For both CoO_2 and Co_3O_4 , we have optimized their internal structural parameters. We can see that although much more localized, the *d* DOS of Co^S in

FIG. 3. The calculated density of *d* states of Co in CoO_2 , Co_3O_4 , and various cases of Codoped TiO₂ rutile. Dotted vertical lines denote the Fermi energy.

Ti₁₅Co₁O₃₂ resembles that of Co in CoO₂ in both the exchange splitting and crystal field splitting, suggesting they are in a +4 oxidation state. In an octahedral field, t_{2g} is lower than e_g , and thus Co⁴⁺ will have a spin magnetic moment of 1 μ_B . As for the combination 2Co^S+Co^I, a close resemblance can be found between Co^S(Co^I) in TiO₂ rutile and Co^B (Co^A) in Co₃O₄. It thus provides strong evidence that Co^S and Co^I in such a combination are in +3 and +2 oxidation states, respectively. The six *d* electrons of Co^S just fill t_{2g} states, and thus yield a vanishing spin magnetic moment. Unlike the interstitial Co in anatase and Co^A in Co₃O₄, Co^I in TiO₂ rutile is in an octahedral field; therefore the lone electron in the e_g state gives a spin moment of 1 μ_B .

In summary, our *ab initio* density functional theory study reveals that in Co-doped rutile TiO_2 , Co can occupy inter-

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- ¹H. Ohno, Science **281**, 951 (1998).
- ²Y. Ohno, D. K. Young, B. Beschoten, F. Matsukura, H. Ohno, and D. D. Awschalom, Nature (London) **402**, 790 (1999).
- ³S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488 (2001).
- ⁴G. A. Medvedkin, T. Ishibashi, T. Nishi, K. Hayata, Y. Hasegawa, and K. Sato, Jpn. J. Appl. Phys., Part 2 **39**, L949 (2000).
- ⁵S. Choi, G. B. Cha, S. C. Hong, S. Cho, Y. Kim, J. B. Ketterson, S. Y. Jeong, and G. C. Yi, Solid State Commun. **122**, 165 (2002).
- ⁶S. Cho, S. Y. Choi, G. B. Cha, S. C. Hong, Y. K. Kim, Y. J. Zhao, A. J. Freeman, J. B. Ketterson, B. J. Kim, Y. C. Kim, and B. C. Choi, Phys. Rev. Lett. 88, 257203 (2002).
- ⁷Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Y. Koshihara, and H. Koinuma, Science **291**, 854 (2001).
- ⁸S. A. Chambers, S. Thevuthasan, R. F. C. Farrow, R. F. Marks, J. U. Thiele, L. Folks, M. G. Samant, A. J. Kellock, N. Ruzycki, D. L. Ederer, and U. Diebold, Appl. Phys. Lett. **79**, 3467 (2001).
- ⁹M. S. Park, S. K. Kwon, and B. I. Min, Phys. Rev. B 65, 161201 (2002).
- ¹⁰D. H. Kim, J. S. Yang, K. W. Lee, S. D. Bu, T. W. Noh, S.-J. Oh, Y.-W. Kim, J. S. Chung, H. Tanaka, H. Y. Lee, and T. Kawai, Appl. Phys. Lett. **81**, 2421 (2002).
- ¹¹W. T. Geng and K. S. Kim, cond-mat/0306389 (unpublished).
- ¹²M. S. Park, S. K. Kwon, and B. I. Min, Physica B **328**, 120 (2003).
- ¹³Y. Matsumoto, M. Murakami, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, K. Nakajima, T. Chikyow, and H. Koi-numa, Appl. Surf. Sci. **189**, 344 (2002).

stitial sites, upon clustering of substitutional Co. As a result, a reference bulk system used to extract information on the local structure of Co in a polycrystalline material should be one that containing both substitutional and interstitial Co. It is found that the interstitial Co destroys the spin polarization of the neighboring substitutional impurities by lowering its charge state, and therefore plays an important role in the magnetic structure of such a material.

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- ¹⁴W. K. Park, R. J. Ortega-Hertogs, J. S. Moodera, A. Punnoose, and M. S. Seehra, J. Appl. Phys. **91**, 8093 (2002).
- ¹⁵ Y. L. Soo, G. Kioseoglou, S. Kim, Y. H. Kao, P. Sujatha, J. Parise, R. J. Gambino, and P. I. Gouma, Appl. Phys. Lett. **81**, 655 (2002).
- ¹⁶G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11 169 (1996).
- ¹⁷D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
- ¹⁸J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B 46, 6671 (1990).
- ¹⁹R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1960).
- ²⁰J. Goniakowski, J. M. Holender, L. N. Kantorovich, M. J. Gillan, and J. A. White, Phys. Rev. B **53**, 957 (1996).
- ²¹ P. Mahadevan and A. Zunger, Phys. Rev. Lett. **88**, 047205 (2002).
- ²²X. Luo, S. B. Zhang, and S.-H. Wei, Phys. Rev. Lett. **90**, 026103 (2003).
- ²³J. Xie and S. P. Chen, Phys. Rev. Lett. 83, 1795 (1999).
- ²⁴ CRC Handbook of Chemistry and Physics (CRC Press, Boca Raton, FL, 1995).
- ²⁵N. W. Ashcraft and N. D. Mermin, *Solid State Physics* (Harcourt, Orlando, FL, 1976), p. 681.
- ²⁶ P. W. Anderson, Phys. Rev. **79**, 350 (1950).
- ²⁷B. E. Larson, K. C. Hass, H. Ehrenreich, and A. E. Carlsson, Phys. Rev. B **37**, 4137 (1988); B. E. Larson and H. Ehrenreich, *ibid.* **39**, 1747 (1989).
- ²⁸J. Blinowski, P. Kacman, and J. A. Majewski, Phys. Rev. B 53, 9524 (1996).
- ²⁹H. Saito, W. Zaets, and S. Yamagata, Y. Suzuki, and K. Ando, J. Appl. Phys. **91**, 8085 (2002).
- ³⁰G. G. Amatucci, J. M. Tarascon, and L. C. Klein, J. Electrochem. Soc. **143**, 1114 (1996).