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Defect compensation, clustering, and magnetism in Cr-doped anatase TiO_2

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The origin of the magnetism in recently reported Cr doped anatase TiO_2 is investigated with first principles full-potential linearized augmented plane wave calculations. Through a systematic study over a range of defect compensation, we predict a strikingly different behavior of Cr^{3+} (compensated species) and Cr^{4+} (noncompensated species): Cr^{3+} tends to distribute uniformly but contributes only to paramagnetism. By contrast, Cr^{4+} tends to form clusters which induces strong ferromagnetism. The same *p-d* hopping interaction found in Mn:GaAs also explains the presence or absence of ferromagnetism and its dependence on the compensation; this short-range bonding interaction is also one of the major sources for the predicted clustering of Cr^{4+}. Our results thus contradict the experimental interpretation that oxygen vacancies induced the ferromagnetic coupling between Cr^{3+} through the F-center bound magnetic polaron (FCBMP) mechanism. We show that large size magnetic polarons cannot form in $Cr:TiO_2$ and that the FCBMP mechanism does not apply.

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In the pursuit of high T_c dilute magnetic semiconductors (DMS), the discovery of room temperature ferromagnetism in transition metal doped TiO_2,[1] ZnO,[2] and SnO_2 (Ref. 3) has aroused a great deal of research interest. Despite numerous experimental and theoretical efforts, the mechanism for the strong ferromagnetism in these oxide DMS is still unresolved. Recently, Coey *et al.* proposed an F-center bound magnetic polaron (FCBMP) mechanism[4] which could mediate ferromagnetic interaction between the transition metal dopants in TiO_2, ZnO, and SnO_2. In their theory, the donor electrons are weakly bound to the hydrogenic orbits of the F centers. Due to the large dielectric constants of these oxides, the donor electron states are rather extended to cover a number of dopant atoms, and thus provide an indirect ferromagnetic interaction between them. The FCBMP theory was applied[4] to explain the chemical trend of a series of transition metal-doped ZnO materials, as well as the magnetism in ZnO:Sc and HfO_2 as d^0 systems.

Recently, the FCBMP theory was employed to explain the ferromagnetism in Cr-doped anatase TiO_2, a new high T_c DMS, with oxygen vacancies as the active F centers.[5] For the well-known $Co:TiO_2$ DMS case, it was also believed[6] that the oxygen vacancies played the vital role for the ferromagnetism through the FCBMP mechanism. At first sight, one may think that these two TiO_2 based DMS are essentially different since $Cr:TiO_2$ is insulating while $Co:TiO_2$ was initially reported to be metallic.[1] Very recently, however, Griffin *et al.* showed that $Co:TiO_2$ can also be made insulating, while still maintaining its high temperature ferromagnetism.[7] It is thus very likely that both DMS share the same mechanism for the strong ferromagnetism, which is not related to free carriers. Interestingly, in $Co:TiO_2$, the Co chemical valence was consistently measured to be 2+ instead of 4+, independent of whether the sample is metallic[8] or insulating.[7] Similarly, the chemical valence of Cr in $Cr:TiO_2$ was not found to be 4+ either, but 3+,[5] implying strong defect compensation in both DMS due to the *n*-type character of the TiO_2 host.

To check whether the oxygen vacancies really induce the ferromagnetism through FCBMP, we performed detailed first principles calculations to study the effect of compensation in $Cr:TiO_2$. We find that (i) strong ferromagnetism can only exist among uncompensated Cr^{4+} species through the *p-d* hopping interaction[9,10] with clustering.[11,13] (ii) The fully compensated Cr^{3+} species is magnetically inactive and only contributes to paramagnetism. As compensation increases, the ferromagnetism is constantly weakened. (iii) Contrary to the experimental interpretation,[5] oxygen vacancies do not induce ferromagnetism but actually destroy it. (iv) Since $Cr:TiO_2$ is dominated by charge transfer, large size magnetic polarons cannot form which excludes the possibility of FCBMP as the origin of the observed ferromagnetism.

The *ab initio* calculations are performed with the highly precise full-potential linearized augmented plane wave (FLAPW) method[14] with optimized atomic positions. As indicated by the experiments,[5] most Cr atoms occupy substitutional sites; a smaller number may go into the interstitial and act as donors. Other donor species include oxygen vacancies and Ti interstitials, which we take to be general donor defects that shift the Fermi level, and affect the properties of the DMS. We use a 48-atom supercell in our calculations. With one or two substitutional Cr, the simulated doping level is 6.25% and 12.5%, respectively, which lies within the experimental concentration range.[5] For the exchange correlation potential, we use the GGA of Perdew-Burke-Ernzerhof.[15] Brillouin zone integrations are performed by summations over a $4\times4\times4$ Monkhorst-Pack special *k* point mesh.[16]

We first consider an isolated substitutional Cr in TiO_2; its band structure is shown in Fig. 1. For pure anatase TiO_2, the experimental band gap is 3.2 eV, while our FLAPW calculation based on density functional theory (DFT) underestimates it (as expected) to be 2.0 eV. Through doping, three t_{2g} bands are introduced into the gap region, but in only one spin channel. Therefore $Cr:TiO_2$ belongs to the so-called half-metallic ferromagnets with the crystal field splitting and the exchange splitting both exceeding 1 eV. These t_{2g} states lie about 1 eV above the valence band maximum (VBM). As-grown anatase TiO_2 is an *n*-type semiconductor due to the presence of shallow donors. Through Cr doping, the *n*-type carriers are transferred to the low-lying Cr 3*d* states,

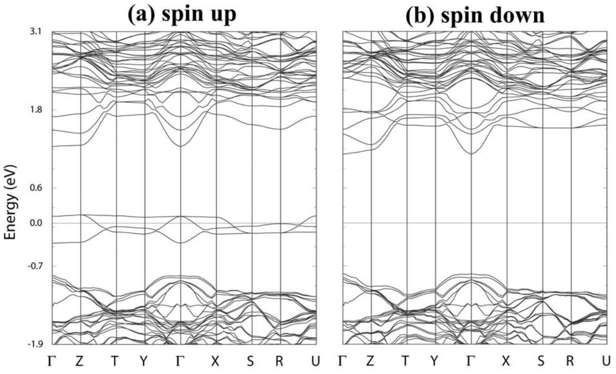

FIG. 1. (a) Spin-up band structures and (b) spin-down band structures of a single substitutional Cr^{4+}. The system is half metallic with a magnetic moment of $2\mu_B$ per Cr.

which are then tightly bound to the Cr sites. This charge transfer is responsible for the insulating behavior of $Cr:TiO_2$.

In the absence of defects, the band structure in Fig. 1 implies that each Cr has two $3d$ electrons and thus has a magnetic moment of $2\mu_B$ with a chemical valence of 4+. As defect compensation goes up, the Cr^{4+} are gradually turned into Cr^{3+} due to charge transfer. Although fractional chemical valences may be more appropriate for Cr due to some covalent nature of the Cr-O bond, this quantitative ambiguity in the assignment of the Cr chemical valences does not affect the main physics in this paper. Nevertheless, throughout this paper, Cr^{4+} should be more strictly understood as the "noncompensated species," with Cr^{3+} as the "fully compensated species."

Through defect compensation, the extra electrons filling the third Cr t_{2g} state could come from oxygen vacancies or Cr interstitials. On the other hand, Ti interstitials in $Cr:TiO_2$ should not exist in as large an amount as in the case of pure TiO_2, since otherwise there will be a natural tendency for the substitutional Cr to exchange positions with the interstitial Ti, pushing Ti interstitials back to the lattice sites, as in the case of $Co:SnO_2$.[3] Indeed, we found a total energy decrease by 0.3 eV if a substitutional Cr exchanges its position with an interstitial Ti. Experimentally, only Cr^{3+} was detected so far.[17] It was therefore proposed that there are half as many oxygen vacancies, which serve as compensation sources and mediate the ferromagnetism through FCBMP.[5]

To check these conjectures, we studied three structures corresponding to different levels of defect compensation: (i) In the noncompensated limit, there are two substitutional Cr in our supercell. (ii) In the fully compensated limit where the FCBMP is believed to operate, an oxygen vacancy is added. (iii) To simulate the partially compensated situation where the third t_{2g} state is partially occupied, we put in an (interstitially placed) Li atom in addition to the existing two substitutional Cr. The Fermi level in each case is shown in Fig. 2: point *A* corresponds to the noncompensated limit; between points *A* and *B* the system is partially compensated; beyond point *B*, the system is fully compensated with E_F now lying in an energy gap; E_F cannot be lower than point *A* since there is no apparent acceptor level that is deeper than the Cr t_{2g} states. On the other hand, it cannot be higher than point *C*, which is the conduction-band minimum, since otherwise the system will become metallic, which contradicts the insulating behavior of $Cr:TiO_2$.

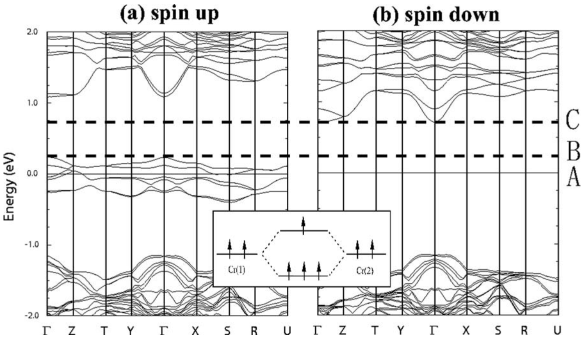

FIG. 2. Band structure with two substitutional Cr^{4+}. Points *A*, *B*, *C* indicate the position of E_F with different compensation levels: (A) noncompensation; (B) partial compensation; (C) full compensation. The inset shows the *p*-*d* hopping interaction model.

Figure 2 presents the band structure of two Cr atoms with a Cr-Cr distance of 10.3 a.u., the largest possible distance allowed by the size of our supercell. The six t_{2g} bands come from the two Cr atoms, but with strong hybridization between them. Since with two Cr's the system is still half metallic, this hybridization virtually provides a ferromagnetic interaction between the two Cr's. Consequently, the ferromagnetic (FM) state is found to be lower in total energy than the antiferromagnetic (AFM) state by 38 meV. Such a bonding interaction involves the $2p$ states of the oxygen atoms lying between the two Cr's and is called the "*p*-*d* hopping interaction," which was initially proposed[10] to explain the FM in Sr_2FeMoO_6. In the "classical" DMS of Mn:GaAs, such a *p*-*d* hopping interaction is also employed to explain the FM which shows an unusual directional dependence.[9] Depending on whether there are holes or not, the *p*-*d* hopping interaction can stabilize either the FM or AFM states for a series of transition metals doped in GaAs. Below, we will show that this *p*-*d* hopping interaction can explain equally well the FM in $Cr:TiO_2$ and its dependence on compensation.

In Fig. 3 we focus on the six t_{2g} bands at different compensation levels. These bands are decomposed into the relative contributions from the two Cr's. For the noncompensated case [Figs. 3(a) and 3(b)], all the band states have almost equal contributions from both Cr's, showing the strong coupling of their $3d$ states. As the compensation level goes up [Figs. 3(c) and 3(d)], some band states start to show the dominant contribution from one Cr, with a negligible contribution from the other, implying a decoupling tendency due to defect compensation. The most drastic change is found in the fully compensated case [Figs. 3(e) and 3(f)]: when all the t_{2g} states are fully occupied, almost all the t_{2g} states are fully decoupled, indicating that the *p*-*d* hopping interaction vanishes and so no longer provides a strong Cr-Cr FM interaction. Indeed, the total energy difference between the FM and the AFM states drops to 24 meV at partial compensation, and virtually to zero in the full-compensation case—which predicts a PM (paramagnetic) state. The systematic decrease of coupling with increasing compensation

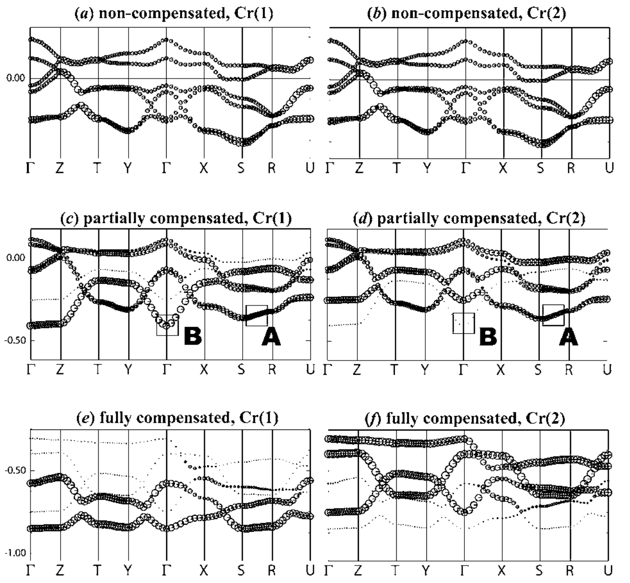

FIG. 3. Band-character decomposition of the t_{2g} states for the two Cr atoms, shown as the dependence on the compensation levels. In each panel of a Cr atom, the size of the circles is proportional to the $3d$ character of that Cr. For the partially compensated case, the squares A and B are used to illustrate typical coupled (A) and decoupled (B) $3d$ states between the two Cr's.

can be easily understood by the p-d hopping interaction model shown schematically in the inset to Fig. 2: when the third Cr t_{2g} state is empty, there is an energy lowering due to the formation of the bonding and antibonding states. Since compensation provides extra electrons which gradually populate the antibonding states, such an energy lowering constantly drops until the fully compensated case when all the anti-bonding states are occupied. Therefore, all the Cr t_{2g} states are decoupled—which wipes out the FM interaction.

Our simulation of the fully compensated case provides a scenario of how the oxygen vacancies affect the magnetic interaction. If there were really half as many oxygen vacancies as the number of Cr dopants at the fully compensated limit, then the oxygen vacancies would destroy the FM. This result is in complete contradiction to the previous declaration[5] that oxygen vacancies promoted FM, and explains why the oxygen vacancy related FCBMP mechanism does not apply to Cr:TiO$_2$: the FCBMP mechanism assumes a strong hybridization between the donor electron and the transition metal $3d$ states by which a polarized impurity band around E_F is formed.[4] As shown in Fig. 1, the calculated Cr t_{2g} states appear at about 1 eV above the VBM, which agrees with the x-ray photoemission spectroscopy (XPS) valence spectra[18] despite the DFT underestimate of the band gap by 1.2 eV. With the oxygen vacancy as a shallow donor, its induced defect states are well separated from the Cr t_{2g} states by $\geqslant 1$ eV. Therefore charge transfer effects dominate, which excludes strong hybridization and forbids the formation of large size magnetic polarons. Since the donor electrons will be tightly bound to the Cr sites, their wave functions cannot cover a number of magnetic ions, which means the FCBMP mechanism does not work in Cr:TiO$_2$.[12]

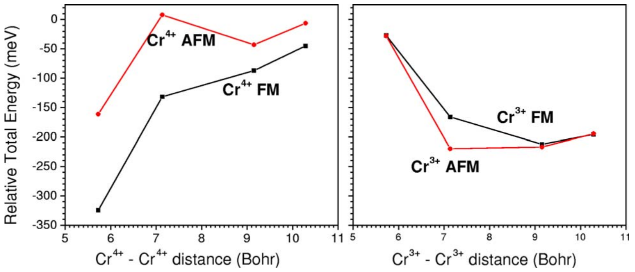

FIG. 4. (Color online) Total energy vs the Cr-Cr distance for (a) noncompensated (Cr^{4+}) and (b) fully compensated (Cr^{3+}).

According to the inset to Fig. 2, the p-d hopping interaction provides an effectively attractive interaction between the transition metal dopants when the antibonding states are not fully occupied. Indeed, in Fig. 4(a), such a "clustering effect"[11] is identified at the noncompensated limit: when the Cr^{4+} pair moves closer, the bonding interaction becomes stronger and the total energy decreases monotonically. On the other hand, since compensation weakens the p-d hopping interaction, it is expected that the clustering tendency should decrease with compensation, and eventually disappear at the fully compensated limit. This proves to be true for Cr^{3+}: the attraction is now replaced by repulsion between the fully compensated Cr^{3+}, as is clearly seen in Fig. 4(b).

In Fig. 4(a), the clustering effect exists in both the FM and AFM states of Cr^{4+}. This fact implies, that there is another source of clustering besides the major contribution from the p-d hopping interaction: in the AFM states, the p-d hopping process happens between the majority spin of one Cr^{4+} and the minority spin of the other. Therefore, it must overcome the large exchange splitting ($\geqslant 1$ eV) of Cr:TiO$_2$. Such a weak hopping interaction is not expected to contribute much to the clustering in the AFM states of Fig. 4(a). Thus, the spin-independent Coulomb interaction also affects the clustering: it contributes a minor part to the attraction of Cr^{4+}, but becomes dominant for the repulsion of Cr^{3+} as electrons accumulate on the Cr sites. This may be different from the GaAs DMS family, where it is believed that the p-d hopping interaction is the only important source to induce the clustering effect of the transition metal dopants.[13]

The dependence of the magnetic interactions with the Cr-Cr distances in Fig. 4 shows the sharp contrast between Cr^{4+} and Cr^{3+}: while Cr^{4+} pairs are always coupled FM, which can be very strong at close distances, Cr^{3+} never shows any sign of FM: it remains PM even at the closest Cr-Cr distance of 5.73 a.u.. The only appreciable magnetic interaction between Cr^{3+} pairs (about 50 meV at 7.14 a.u.) is instead AFM. The slightly favorable AFM ground state for Cr^{3+}, as well as its directional dependence (at 7.14 a.u., the two Cr atoms are connected by the strongest $3d$-$2p_{\pi}$-$3d$ bonding) is fully consistent with the p-d hopping interaction model.[9] Further, our exhaustive search for possible FM ground states with varied positions for the Cr^{3+} pair and the oxygen vacancy (in 20 configurations) has not been successful. Therefore, we conclude that Cr^{3+}, as the dominant species identified by the XPS (Ref. 18) and the x-ray absorption near-edge structure (XANES) measurements,[5] is in fact pulse modulated paramagnetic (PM) instead of FM. The observed FM in Cr:TiO$_2$ should come from some remanent Cr^{4+} ions that were not fully compensated during the fabrication process.[17]

Finally, while theoretically the magnetization per Cr is expected to be $2\mu_B$ (for Cr^{4+}) or $3\mu_B$ (for Cr^{3+}), the experiments, however, gave only about $0.6\mu_B$ Cr.[5] This is further evidence that indeed the majority Cr species (Cr^{3+}) does not contribute to FM. The only Cr species which could induce FM is Cr^{4+}. Since 3+ is the most stable chemical valence state of Cr as in Cr_2O_3, it actually means that the FM in $Cr:TiO_2$ is metastable. These predictions have now been strongly supported by the newest experiments,[19] which show that the FM is crucially dependent on the growth speed: the slow-grown $Cr:TiO_2$ samples are structurally perfect and are indeed found to be PM. On the other hand, FM is clearly associated with the Cr dopants, but is only identified in fast-grown samples which are more structurally defective.[19] With slow-growth speed, the surface atoms have sufficient diffusion to thermodynamic equilibrium, which explains why most Cr ions are fully compensated. It seems very likely that a small amount of Cr^{4+} were not compensated in the fast-grown samples which induced the strong FM (Ref. 5) through clustering. They may well be seen with electron-energy-loss spectroscopy (EELS) measurements, as in the case[20] of $Co:TiO_2$.

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