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Ferromagnetism in HfO_2 induced by hole doping: First-principles calculations

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According to recent reports of the unexpected magnetism discovered in thin films of HfO_2, a set of first-principles calculations is carried out on the hole-doped HfO_2 system with nonmagnetic ions. It is found that the holes are doped into the p bands of the oxygen atoms near the dopant, which form a nearly planar trigonal structure with their nearby three Hf atoms surrounding them. The doped holes will make the p bands spin split. In addition, the total number of Bohr magneton in the supercell is equal to the number of doped holes by keeping the system in high spin state. Our results show that ferromagnetism in the oxygen p orbital induced by hole doping is quite possible and is a general phenomenon in ionic oxides, which would be a possible way to find new ferromagnetic materials or half-metals in nonmagnetic d^0 composites.

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Recently, ferromagnetism was unexpectedly discovered in the thin films of the pure dielectric oxide HfO_2,[1] where both Hf^{4+} and O^{2-} are nonmagnetic ions. The d and f shells of the Hf^{4+} ion are either empty or full, and no other transition metal is doped. Thus, the local moment is not likely the origin of the observed ferromagnetism. One possible mechanism proposed for the observed magnetism is the intrinsic oxygen vacancies, which act as a donor, leading to the n-type doping of the material. The mixing of the impurity band with the empty $5d$ states of the Hf^{4+} ion would transfer some electrons to the d orbital, resulting in the polarization of the impurity bands and thus the ferromagnetism.

On the other hand, the first-principles calculations[2] show that the hafnium vacancy is another reason for the observed ferromagnetism in the pure HfO_2, instead of the oxygen vacancy. The introduced holes by Hf vacancies form the high-spin defect states, causing the ferromagnetic (FM) order in the system. However, further experiment[3] argues that the hafnium vacancies are less likely than the oxygen ones due to the high charge state. It is also found that most of the ferromagnetism in HfO_2 is induced from the surface or the interface with the substrates instead of the bulk. In fact, one should expect that there should be some elements in the substrate or some vacancies doped into the HfO_2 layers around the interface or surface. One of the substrates used in experiment is sapphire. Hence, the effect of introduced holes by Al in HfO_2 should be considered. On the contrary, Abraham *et al.* recently questioned the observed ferromagnetism in the HfO_2, ascribing it to the contamination of the sample by stainless-steel tweezers. They further stated that handling of silicon with tweezers can cause significant contamination of the surface over a wide area.[4] However, the effect of ferromagnetism in HfO_2 is not only observed in the case of silicon substrates, but also in sapphire and yttria-stabilized zirconia cases.[3] And no ferromagnetism is found in the similar prepared zinc or tin oxides.[1] Furthermore, plastic tweezers are often used in the practice[5] and the magnetic moment does not scale with the film thickness. Thus, the origin of the observed ferromagnetism in HfO_2 could not be simply ascribed to the contamination of the sample, and needs more extensive study experimentally and theoretically.

In this paper, the substitution of the nonmagnetic element, i.e., K, Sr, Al, and vacancy for Hf is considered in order to study the dependence of the magnetism on the number of doped holes since the vacancy and K, Sr, and Al have four, three, two, and one fewer valence electrons, respectively, compared with Hf. It is found that the HfO_2 becomes FM after being doped by above elements and vacancies, which is similar to the effect of cation vacancies in some nonmagnetic oxides, such as CaO and MgO.[6] In the monoclinic HfO_2, there are two types of oxygen sites, one (labeled as O3) is surrounded by three Hf atoms, forming a nearly planar trigonal structure with a slightly deformed D_{3h} symmetry as shown in Fig. 1(a). The other (labeled as O4) is bonded with four Hf atoms, forming a deformed tetrahedron.[2,13] The analysis of the electronic structures shows that the doped holes will go into the p bands of O3, making them spin split. The magnetic moment on O3 is more than 0.1 μ_B/atom for those very close to the dopant, which decreases to the order of 0.01 μ_B/atom for the other O3 atoms. The O4 atoms al-

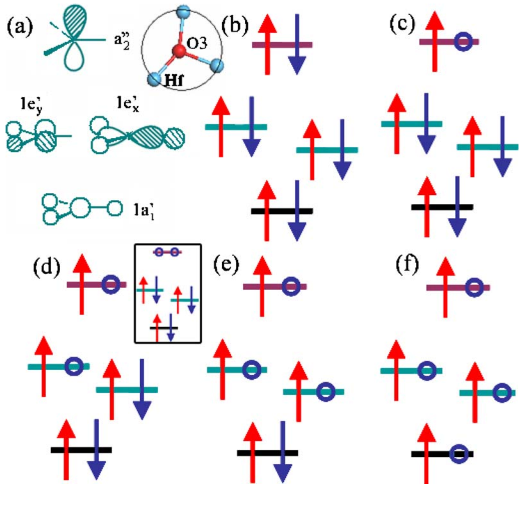

FIG. 1. (Color online) (a) The geometry of planar oxygen O3 in the monoclinic HfO_2 and its ideal bonding states under the perfect D_{3h} symmetry. The energy level diagram and spin configuration for (b) pure, and doped monoclinic HfO_2 with (c) one hole, (d) two holes, (e) three holes, and (f) four holes. The inset in (d) is another possible configuration in the case of two holes.

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ways have magnetic moment in the order of 0.001 μ_B/atom. It is found that the doped systems have the lowest energy when the magnetic moment on O3 are parallel, indicating the system tends to be in the high spin state. The total number of Bohr magnetons in a supercell equals to that of doped holes. This kind of hole-induced ferromagnetism should give some hints to understand the ferromagnetism in carbon[7] system and the unusual large magnetic moment on Co ions in the Co-doped SnO_2[8,9] system.

In the present calculations, Vienna Ab Initio Simulation Package plane-wave code[10] is employed. The electron-ion interactions are described by projector augmented wave version of pseudopotentials[11] and the exchange correlation term is treated within the generalized gradient approximation as parametrized by Perdew and Wang.[12] The $5p$ electrons of hafnium atom is treated as the valance state during the generation of pseudopotential. The electron configuration of O, K, Sr, and Al are taken as $[\mathrm{He}]2s^22p^4$, $[\mathrm{Ne}]3s^23p^64s^1$, $[\mathrm{Ne}]3s^23p^64s^2$, and $[\mathrm{Ne}]3s^23p^1$, respectively, where the core electron configurations are shown in the square brackets represented by the inert element. In the calculations, a supercell of $2\times2\times2$ monoclinic unit cell is used,[13] which totally contains 96 atoms. The monoclinic structure is used since it is the structure observed in the experiment.[1] One Hf is replaced by K, Sr, Al, or vacancy in the supercell to simulate the different doping cases with the concentration of 3.125%. For this kind of supercell, a kinetic-energy cutoff of 500 eV and totally 4 nonequivalent k-points in the first Brillouin zone are used in the total energy calculations.[13] The positions of atoms are relaxed until the forces on them are less than 0.05 eV/Å.[2,13]

In the monoclinic HfO_2, the p electrons of planar O3 form both σ and π bonds with the surrounding $5s$ and $5d$ electrons of the Hf atoms. If the O3 and the Hf atoms form a perfect D_{3h} symmetry structure, the fully occupied O3 bonding orbitals could be schematically shown in Fig. 1(a). The two $2s$ electrons of O3 take the $1a_1'$ orbital, and four of its $2p$ electrons occupy the in-plane $1e_x'$ and $1e_y'$ orbitals, forming the three σ bonds with the three surrounding Hf atoms. The left two p electrons lie in the orbital perpendicular to the plane, forming the π bonds in a_2'' symmetry. However, in the real monoclinic system, the two p orbitals forming the σ bonds are a little nondegenerate because the surrounding Hf atoms are slightly deviated from the D_{3h} symmetry.[2] The O4 atom mostly has the sp^3 hybridization with the Hf atoms, forming four nearly equivalent σ bonds. The difference between O3 and O4 can be seen from their partial densities of states (DOSs) of p orbitals, as shown in Fig. 2. The p electron distribution of O3 is clearly different from that of O4 since the latter is more uniform in energy space. This difference is especially obvious and important in a short energy range below the Fermi level, as indicated by the vertical dash-dotted line at about −0.5 eV in Fig. 2. Once the hole is introduced, it should first go into the p orbitals of O3 within the approximation of rigid band model. In our supercell with 96 atoms, it is found that within the 0.5 eV energy range just below the Fermi level there are totally about 2.38 more electrons in the p orbital of O3 than in the p orbital of O4.

Thus, it is expected that the partially occupied p band would be spin-split since (1) the Hunds coupling for oxygen is about 2.0 eV.[3] Although it is smaller than the p orbital bandwidth of the O3, both of them are in the same order. When hole is introduced into the p orbital, it might be essential to form the molecular orbitals with parallel spins surrounding the O3 atoms, as pointed out by Coey *et al.*[3] (2) The on-site Coulomb repulsion energy U_{pp} of two holes in an oxygen p orbital is 5–7 eV,[6] which is comparable with the broadest bandwidth of 5.5 eV, making the p band relatively narrow. Thus, the U_{pp} in the O p states will have a great influence on the magnetic moment of the system. It had been found that once there are holes in the oxygen p orbital,[6,14,15] or equivalently, there exists a substantial large partial p orbital components[16,17] in the charge carrier state, the U_{pp} of oxygen p electrons would play a critical role in the system. The magnitude of U_{pp} is even comparable with U in the d orbitals of transition metals.[17] The theoretical results obtained for La_2CuO_4, NiO, MnO,[17] and Sr_2FeMoO_6 (see Ref. 16) by *ab initio* and model[18] calculations including U_{pp} are better consistent with the experimental measurements than those without U_{pp}. According to such a supposition, for obtaining a magnetic ground state of the oxide systems with cation vacancies or holes, the ground state of the charge compensation molecular orbital[2,6] is not required to be orbitally degenerate. The spin splitting of oxygen p orbitals would be possible if substantial holes locate in them and the bandwidth is comparable with the Hunds rule coupling energy and on-site Coulomb interaction.

To confirm this picture, we have performed numerical calculations on the doped HfO_2 with one, two, three, and four holes in the $2\times2\times2$ monoclinic supercell by replacing one Hf with the d^0 elements of Al, Sr, K, and vacancy, respectively. After the atom's positions are relaxed, it is found that

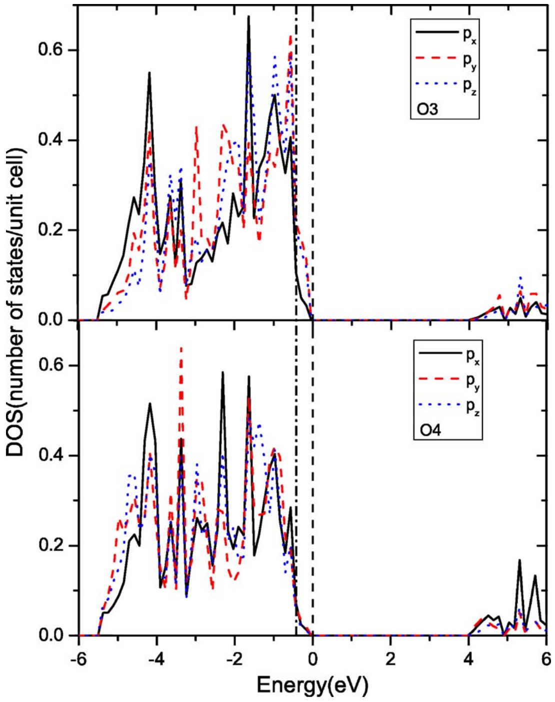

FIG. 2. (Color online) The partial p density of states for the O3 and O4 in the monoclinic HfO_2. The vertical dashed line indicates the Fermi level and the dash-dotted line is explained in the text.

TABLE I. The calculated total energy difference, ΔE (meV), between the nonmagnetic and FM states, and total magnetic moment μ_{tot} (μ_B, in Bohr magneton) per supercell for the different hole-doped HfO_2

	Al	Sr	K	Hf vacancy
ΔE	17.5	28.5	13.0	220.9
μ_{tot}	1.00	1.99	3.00	3.99

the bonds between the O and the doped K and Sr atom are longer than the original Hf-O bond by 0.15–0.30 Å. The Al-O bond is shorter by about 0.20 Å. These results are consistent with the fact that the ionic radii of K^+ (1.51) and Sr^{2+} (1.26) are larger than that of Hf^{4+} (0.83), while Al^{3+}'s (0.54) is smaller. The planar trigonal structure of O3 and the tetrahedron of O4 are found to be nearly unchanged.

In all the four doping cases, the total energy of FM state are lower than the corresponding nonmagnetic state, as shown in Table I. Thus, the hole doping will make the system tend to be in a FM state. The total magnetic moment (in Bohr magnetons) in the supercell is equal to the number of doped holes, though it is unevenly distributed on the oxygen atoms. The magnetic moments on the O3 atoms nearest to the dopant are more than 0.10 μ_B, about one and two orders larger than those on the other O3 atoms and all the O4 atoms, respectively. According to this result and also noticing that the topmost valence bands are composed of O3 *p* electrons, the energy level diagrams for various hole-doped systems could be plotted as shown in Figs. 1(c)–1(f) in a way similar to that in Ref. 2. The case with one hole in Fig. 1(c) is quite easily understood. When two holes coexist, in addition to the $S=1$ configuration shown in Fig. 1(d), there is another possible nonmagnetic configuration ($S=0$), as shown in its inset. Our calculations show that the total energy of $S=1$ FM state is lower than the nonmagnetic state by about 28.5 meV. Thus, the electronic configuration prefers the high spin state to the low one. In fact, because of the Hunds rule coupling energy and the on-site Coulomb repulsion, the nonmagnetic state would be unfavored compared with the magnetic one if the *p* orbital is not fully occupied. Taking into account all these points, we can understand other doping cases quite naturally. For example, in the case of three holes, the three electrons in the *p* orbital tend to form the $S=3/2$ spin state, which, in fact, has lower total energy than those of the $S=1/2$ and the nonmagnetic state by about 5.1 and 13.0 meV, respectively, although the $S=1/2$ spin configuration is also a local energy minimum.

To further clarify the origin of magnetic moment, the spin-polarized total DOS and partial DOS of the *p* orbital for the O3 and O4 are presented in Figs. 3 and 4 for the Al, Sr, and K doping cases. It is clear that the holes are doped into the *p* orbitals of O3 and the magnetic moment is mostly contributed by the O3 *p* electrons, while the *p* electrons of O4 are more uniformly distributed, consistent with the above hypothesis. The quite low hole concentration in the one-hole doping case makes the system to a FM semiconductor. The higher hole concentration in the case of two doped holes makes the system nearly a FM metal, as shown in the left panel of Fig. 4, while that having three holes in the right panel is a half-metal, which could be understood from the different diagrams shown in Figs. 1(d) and 1(e). The two nearly degenerate in-plane *p* orbitals make the spin-down channel shown in Fig. 1(d) partially occupied, and thus the system is a metal. On the contrast, the large energy gap between the in-plane *p* orbital and the *s* orbital makes the diagram shown in Fig. 1(e) to be half-metal with a band gap in the spin-down channel. The half-metal character in the case of four holes is the same as that obtained in Ref. 2, and its DOS is not shown here. Thus, tailoring the system's properties could be done by tuning its hole concentration. The total DOSs at the Fermi level, $D(E_F)$, in both panels of Fig. 4 are very high, about 100 states/eV/supercell, and the spin exchange splitting I of the band is about 0.1–0.2 eV. Consequently, the Stoner criterion for ferromagnetism, $D(E_F)I > 1$, is satisfied in the hole-doped HfO_2 systems. The itinerant electrons in the relatively narrow oxygen *p* band contribute to the magnetic moment of the system.

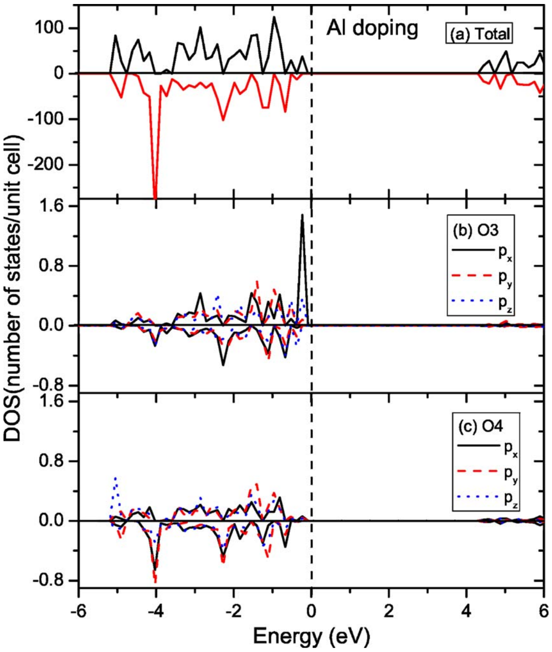

FIG. 3. (Color online) The spin-polarized (a) total and (b) O3 and (c) O4's *p* partial DOS for Al-doped HfO_2. The positive (negative) value means the spin-up (spin-down) DOS. The Fermi level is indicated by the vertical dashed line.

In fact, in addition to the ferromagnetism in CaO induced by Ca vacancy[6] mentioned above, there are also other ionic oxides, such as MgO, MnO, and NiO,[19] in which the oxygen *p* bandwidth is about 3–4.5 eV and the cation vacancy, i.e., the hole doping, can indeed induce the ferromagnetism. However, in the covalent oxides, being different from the ionic materials, the hybridization is very strong, making their bandwidth of the oxygen *p* orbital relatively wider. Thus, the ionic metal oxide could be a proper candidate for the new type of ferromagnetic or spintronic materials. Kenmochi *et al.*[20] have shown that the hole introduced by replacing O with C or N in CaO, MgO, SrO, and BaO would also induce ferromagnetism. In addition, the total number of Bohr magneton in the supercell is also equal to the number of doped

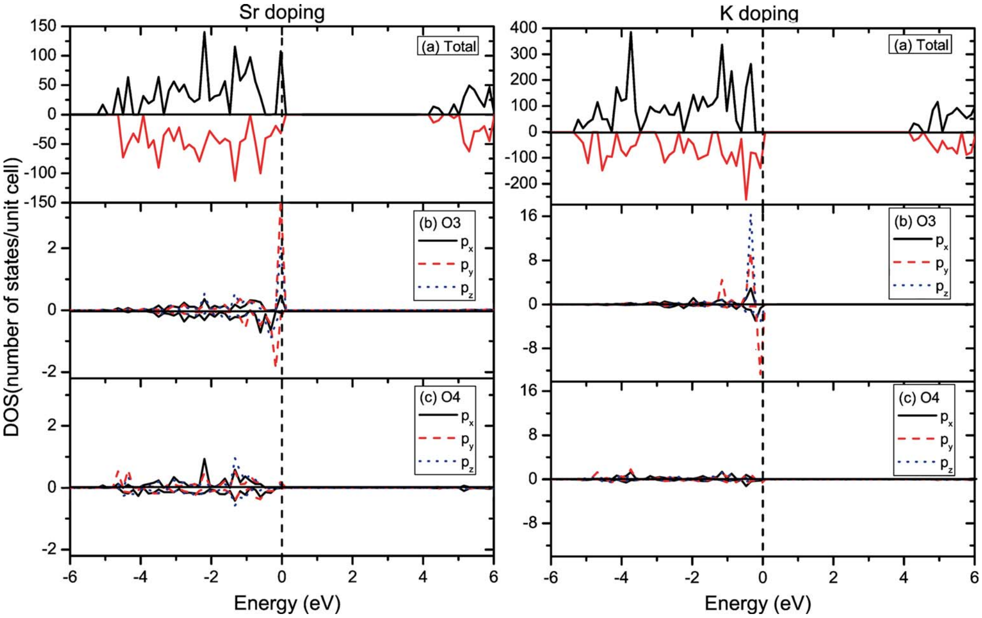

FIG. 4. (Color online) The same as that of Fig. 3, except the left panel is for the Sr doping case and the right panel is for K doping case.

holes, i.e., 2.0 and 1.0 μ_B for C and N doping, respectively, and the Stoner criterion is also satisfied. In the Co-doped ZnO, Spaldin[21] found that two holes introduced by one Zn vacancy would stabilize the FM order and increase its magnetic moment in the supercell from 6.1 to 8 μ_B, in which an additional 1.9 μ_B magnetic moment is contributed by the oxygen atoms. Perhaps, in the Co-doped SnO_2, the observed large magnetic moment on Co atom[8,9] might partially originate from the additional contribution from the oxygen atoms.

In summary, it is found that the holes doped into the HfO_2 could be a possible reason for the observed ferromagnetism in it based on the first-principles calculations. The total number of Bohr magnetons per supercell is found to be equal to the number of doped holes, which distribute mainly on the *p* orbitals of the O3 atoms near to the dopant. The electronic structures show that the Stoner criterion for band ferromagnetism is satisfied and the high spin state of the system is lower in energy. Based upon our discussions, ferromagnetism in the oxygen *p* orbital induced by hole doping is quite possible and is a general phenomenon in ionic oxides. The condition for obtaining the magnetic ground state is not as strict as stated in Ref. 6. It only requires that the system has quite narrow *p* bands near the Fermi level, compared with the Hunds coupling energy and the on-site Coulomb repulsion energy, and the hole is doped into it.

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