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Vacancy-driven ferromagnetism in ferroelectric PbTiO₃

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The possible origin of ferromagnetism in PbTiO₃ containing vacancies is investigated by performing first-principles calculations. We demonstrate that O and Ti vacancies both induce ferromagnetism but by different mechanisms: the ferromagnetism driven by the O vacancy originates from the spin-polarized e_g state of the nearest Ti atom, whereas that driven by the Ti vacancy is due to the half-metallic p_x state of the nearest O atom. The results presented here provide fundamental insights into the design of multiferroics in conventional ferroelectrics. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4704362>]

Ferroelectric PbTiO₃ and its solid solutions, e.g., Pb(Zr,Ti)O₃, possess particularly large spontaneous polarizations and piezoelectric responses. Consequently, they are widely used in technological devices such as nonvolatile random access memories (FeRAMs), transducers, and electromechanical devices.^{1,2} Conventional ferroelectrics, such as PbTiO₃ and BaTiO₃, are well-known to be non-magnetic materials, because the formal d^0 electron configuration (e.g., Ti⁴⁺) in these ferroelectrics obviously contradicts with the partially filled d states required for ferromagnetism.³ In contrast, the existence of weak ferromagnetism was unexpectedly discovered in PbTiO₃ nanoparticles.⁴ Experimental measurements suggest that vacancies included in PbTiO₃ may play a significant role in inducing ferromagnetism.^{5,6} However, the origin of ferromagnetism has yet to be elucidated.

Materials that simultaneously exhibit ferroelectricity and ferromagnetism/antiferromagnetism in the same phase are known as multiferroics. Multiferroics have attracted considerable attention in recent years owing to the additional intriguing feature that the coexisted ferroic properties strongly coupled with each other, i.e., magnetoelectric (ME) coupling. Because the ME coupling enables ferroelectricity (ferromagnetism) to be controlled by applying a magnetic (electric) field, multiferroics have the potential to realize advanced technological devices, such as multiple-state memory elements and new functional sensors.^{7–10} Defective ferroelectric PbTiO₃ that simultaneously exhibits ferromagnetism is one of the good candidates for multiferroics. For the use and applications as multiferroics, it is essential to reveal the detailed origin of ferromagnetism and the electronic-level mechanism.

This letter investigates which, if any, vacancies involves ferromagnetism and provide electronic-level insight into the origin of ferromagnetism in PbTiO₃, by performing first-principles density-functional theory (DFT) calculation. The results obtained here should be promising for materials design of multiferroics.

We perform first-principles spin-density-functional theory calculations implemented in the VASP code^{11,12} using plane-wave basis sets with a cutoff energy of 500 eV. The electron-ion interaction is described by projector-augmented

wave (PAW) potentials¹³ explicitly including the Pb 5*d*, 6*s*, and 6*p*, the Ti 3*s*, 3*p*, 3*d*, and 4*s*, and the O 2*s* and 2*p* electrons in the valance states. A $5 \times 5 \times 5$ Monkhorst-Pack k -point mesh is used for the Brillouin zone integrations. For the simulation model, we employ a $2 \times 2 \times 2$ periodic supercell with 40 atoms in which two perovskite-unit-cells are arranged in each x , y , and z direction.^{14,15} We consider both [100]-polarized tetragonal PbTiO₃ in the ferroelectric (FE) phase and cubic PbTiO₃ in the paraelectric (PE) phase. A vacancy, denoted as V_i ($i = \text{Pb, Ti, O1, and O2}$) is introduced by removing one i atom from the simulation supercell. Note that the oxygens O1 and O2, which are located in the [100] direction and the [010] or [001] direction relative to the Ti atom, respectively, are not equivalent to each other in the ferroelectric phase. The atomic structure is fully relaxed until the Hellmann-Feynman forces drop below 0.01 eV/Å.

Table I lists the magnetic moments M of various vacancies in the tetragonal and cubic PbTiO₃. We find nonzero magnetic moments for the O1 and Ti vacancies in both the phases, i.e., emergence of ferromagnetism, whereas there is no magnetization for the Pb vacancy. The Ti vacancy induces a larger magnetic moment than the O1 vacancy. Moreover, the non-trivial difference in magnetic moments between the FE and PE phases indicates that the ferroelectricity strongly affects the ferromagnetism induced by the vacancies. This fact implies potential magnetoelectric coupling.

Figures 1(a) and 1(b) show the spatial distributions of the magnetization density around the O1 and Ti vacancies, respectively. For the O1 vacancy, the magnetization mainly appears around the V_{O1} site and the nearest-neighbor Ti atoms. Magnetization is particularly localized around the Ti atom, which are strongly bonded with the O1 atom in a perfect crystal. For the Ti vacancy, on the other hand, the magnetization is localized at the neighboring O1 atom. It

TABLE I. Magnetic moment per vacancy M (in μ_B) of various vacancies in the tetragonal (FE) and cubic (PE) PbTiO₃.

	V_{O1}	V_{O2}	V_{Ti}	V_{Pb}
Tetragonal (FE)	0.488	–	1.633	–
Cubic (PE)	1.570	(= V_{O1})	2.223	–

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FIG. 1. Magnetization density distributions around (a) O1 vacancy and (b) Ti vacancy in the (010) plane. The top and bottom panels correspond to the FE and PE phases, respectively.

should be noted that in the FE phase, the magnetization is mainly localized around only one Ti (or O1) atom nearest to V_{O1} (or V_{Ti}), whereas both the two neighboring Ti (or six neighboring O1) atoms carry a large magnetization in the PE phase. This anisotropy in the magnetization density distribution should be due to a ferroelectric displacement along [100]. Thus, the number of atoms carrying the magnetization causes the different magnetic moments of the FE and PE phases.

To give more insight into the origin of ferromagnetism induced by the vacancies, we investigated the electronic density of states (DOS). Total DOS for the perfect and O1-deficient tetragonal PbTiO_3 are shown in Figs. 2(a) and 2(b), respectively. Perfect PbTiO_3 behaves as an insulator with a band gap energy of 1.6 eV. This value agrees well with that found in a previous study¹⁶ but is smaller than the experimental value of 3.5 eV (Ref. 17): this discrepancy is a well-known problem within the framework of the density functional theory. The O1 vacancy causes the Fermi level to shift up and forms a new state near the bottom of the conduction band, indicating an n -type behavior. The DOS just below the Fermi level asymmetrically differs between the majority and minority spins. Thus, this spin-polarized state contributes to ferromagnetism. Figures 2(c) and 2(d) show the projected DOS for the $3d$ states of the Ti atom nearest to V_{O1} , where the magnetization is mainly concentrated. Here, the O_h -type crystal field in the perovskite structure splits the $3d$ orbitals of the Ti atom into two e_g ($d_{x^2-y^2}$ and d_{z^2}) and t_{2g} (d_{xy} , d_{yz} , and d_{zx}) states, which distribute toward the six neighboring O atoms and toward the four neighboring Pb atoms, respectively. The e_g orbital forms the spin-polarized state just below the Fermi level, suggesting a partially filled $3d$ state on the Ti atom, whereas the t_{2g} orbital does not contribute to the state at all. In addition, the magnetization density distribution localized between the Ti and V_{O1} , as shown in Fig. 1(a), corresponds well to the e_g orbital. Therefore, the e_g states of the Ti atom adjacent to V_{O1} makes a dominant contribution to ferromagnetism induced by the O1 vacancy.

FIG. 2. Total electronic DOS for the (a) perfect and (b) O1-deficient tetragonal PbTiO_3 . The projected DOS for (c) t_{2g} and (d) e_g states of the Ti atom nearest to V_{O1} . The red and blue lines, respectively, represent the majority and minority spins, and the solid vertical line indicates the Fermi level.

It should be noted that the $\text{Ti}-e_g$ orbital hybridizes with the $\text{O1}-p_x$ orbital by forming a $p-d\sigma$ bond in perfect PbTiO_3 . Thus, the loss of the σ bond by the O1 vacancy leads to the partially filled spin-polarized $3d$ state. This result agrees well with the experimental fact that Ti^{4+} is reduced to Ti^{3+} in oxygen-deficient octahedra by charge compensation.¹⁸

For the Ti vacancy, on the other hand, the nature of the induced ferromagnetism differs from that of the O1 vacancy: Figures 3(a) and 3(b) show the total DOS for perfect and Ti-deficient tetragonal PbTiO_3 , respectively. The Fermi level for the Ti vacancy shifts down slightly relative to that of the perfect PbTiO_3 . Consequently, the DOS cross the Fermi energy. Interestingly, the majority spin bands for the Ti vacancy are fully occupied and exhibits insulating characteristics with a band gap. On the other hand, the minority spin DOS crosses the Fermi level and exhibits a conductive character. This indicates that the Ti vacancy shows a half-metallic behavior. The small portion of the minority spin DOS appearing just above the Fermi level indicates that there are more majority spins than that of the minority spins, i.e., it is a spin-polarized state. Figures 3(c) and 3(d) plot the projected DOS for the p_x and p_y ($=p_z$ for the tetragonal symmetry) states of the O1 atom nearest to V_{Ti} , respectively. All the $2p$ states of the O1 atom are polarized because the DOS of the majority and minority spins are asymmetric. However, the p_x state exhibits the fully occupied majority spin and the partially filled minority spin states, whereas both the spins are almost fully occupied in the p_y and p_z states. This result suggests that the p_x state of the neighboring O1 atom to V_{Ti} mainly contributes to the magnetization induced by the Ti vacancy. As mentioned above, the $\text{O1}-p_x$ orbital forms a σ

FIG. 3. Total electronic DOS for the (a) perfect and (b) Ti-deficient tetragonal PbTiO_3 . The projected DOS for (c) p_x and (d) $p_y (= p_z)$ states of the O1 atom nearest to V_{Ti} . The red and blue lines, respectively, represent the majority and minority spins, and the solid vertical line indicates the Fermi level.

bond in perfect PbTiO_3 through hybridization with the $\text{Ti}-e_g$ orbital. Hence, the loss of this bond due to the Ti vacancy leads to the half-filled spin-polarized p_x state. A similar trend is found for the same vacancy in BaTiO_3 .¹⁴

The oxygen vacancy is energetically more stable than the Ti vacancy,^{19,20} suggesting that in practical situations, the oxygen vacancy has a larger population than other vacancies. Thus, the O1 vacancy is the main source of the ferromagnetism emerging in PbTiO_3 . This agrees well with the experimental fact that PbTiO_3 annealed in air exhibits a substantially smaller magnetic moment than that annealed in vacuum.⁵

Although Cao *et al.* reported vacancy-induced magnetism in BaTiO_3 ,¹⁴ there are three non-trivial differences between PbTiO_3 and BaTiO_3 : (i) The O2 as well as O1 vacancies drive magnetism in BaTiO_3 . (ii) There is almost no difference in the magnetic moments between FE and PE

BaTiO_3 by the O1 vacancy (1.27 and $1.23 \mu_B$, respectively), while the difference is more pronounced in PbTiO_3 (see Table I). This is because the ferroelectric distortion of FE PbTiO_3 is considerably large, whereas that of FE BaTiO_3 is relatively smaller and much close to the PE structure due to the different bonding nature.²¹ (iii) The t_{2g} state mainly contributes to magnetism by the O1 vacancy in BaTiO_3 , while the e_g state does for PbTiO_3 .

In summary, the origin of ferromagnetism emerging in PbTiO_3 with vacancies, and its electronic-level mechanism were investigated by performing first-principles DFT calculations. We demonstrated that O and Ti vacancies both induce ferromagnetism but by different mechanisms: the ferromagnetism induced by the O vacancy originates from the spin-polarized e_g state of the nearest Ti atom, whereas that driven by the Ti vacancy is due to the half-metallic p_x state of the O atom nearest to the Ti vacancy. The results presented here provide fundamental insights for the future design of multiferroic materials by conventional ferroelectrics.

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¹⁵The use of a larger $3 \times 3 \times 3$ periodic supercell does not appreciably affect the results because the effect of vacancy is well-confined within two lattices. In fact, the $2 \times 2 \times 2$ supercell has been commonly used for the vacancy in perovskite oxides.

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