



First-principles study on ferromagnetism in double perovskite $\text{Sr}_2\text{AlTaO}_6$ doped with Cu or Zn at B sites



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ABSTRACT

The possibilities of ferromagnetism induced by nonmagnetic dopants (Cu, Zn) in double perovskite $\text{Sr}_2\text{AlTaO}_6$ at B sites are investigated by density functional theory. Calculations reveal that substitutions at Ta-site tend to form high spin electronic configurations and could induce ferromagnetism which can be attributed to the hole-mediated p - d hybridization between Cu (or Zn) e_g states and the neighboring O 2p states. The dopants preferably substitute at Al-site and adopt low spin electronic structures. Due to the smaller hole concentration and weaker covalent intensity, $\text{Sr}_2\text{AlTaO}_6$ with dopants at Al-site exhibits p -type metallic semiconductors without spin polarization.

1. Introduction

Dilute magnetic semiconductors (DMSs) have elicited much attention because of their potential applications in spintronic devices, which combine the charge and spin property of electrons in the materials [1,2]. During past years, a great number of experimental works have reported the above room temperature ferromagnetism by doping the semiconductor with a small quantity of transition metal(TM) atoms, such as Cr-doped ZnTe and AlN [3,4], TMs-doped In_2O_3 [5], TiO_2 [6], and ZnO [7]. However, the origin of the ferromagnetism observed in TM doped semiconductors is still under debate [8]. Furthermore, because of the limited solubility of TM impurities in particular hosts, the formation of nanoscale regions containing a large density of magnetic clusters, precipitates or ferromagnetic secondary phases have also been detected in some TM doped DMSs [9,10], which would rule out most practical applications. To avoid the secondary magnetic phase and the magnetic ions clustering, studies on DMSs obtained by doping intrinsic nonmagnetic elements, such as carbon, nitrogen and copper, have been reported theoretically and experimentally [11–13]. But up to now, few works have been focused on the magnetism of nonmagnetic element substitution for cationic sites in DMSs.

Since the observation of the room-temperature colossal magnetoresistance phenomenon in $\text{Sr}_2\text{FeMoO}_6$ [14,15], intensive research efforts have been devoted to understanding electronic and magnetic properties of double perovskite with $\text{A}_2\text{B}'\text{B}''$ formula unit. The ideal structure of double perovskite $\text{A}_2\text{B}'\text{B}''\text{O}_6$ consists of corner sharing octahedral $\text{B}'\text{O}_6$ and $\text{B}''\text{O}_6$, with 12-coordinated interstitial spaces between octahedra occupied by the A-site cations. This structure possesses cubic symmetry with space group $Fm\bar{3}m$ (No. 225). However, the size mismatch between the octahedral network and A-site cations leads to the octahedral tilting distortions, which lowers the cubic symmetry of double perovskites. The choice of suitable elements A, B' and B'' can achieve various applications such as in the fields of spintronics ($\text{Sr}_2\text{FeMoO}_6$ [14] and $\text{Sr}_2\text{FeReO}_6$ [16]), multiferroicity ($\text{Ba}_2\text{NiMnO}_6$ [17]), magnetodielectric materials ($\text{La}_2\text{NiMnO}_6$ [18,19]) and magneto-optic devices ($\text{Sr}_2\text{CrReO}_6$ and $\text{Sr}_2\text{CrOsO}_6$ [20]).

Complex tantalum oxides have been of interest for their photocatalytic activity [21,22], ferroelectric behavior [23] and their dielectric properties [24], while double perovskite oxide $\text{Sr}_2\text{AlTaO}_6$ (SAT) has usually been used as thin film substrates in many experimental researches [25,26]. Recently, the structural, dielectric and catalytic properties of the double perovskite-type oxides with the general for-

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mula A_2AlTaO_6 ($A = Ca, Sr, Ba$) were investigated [27], where it was found that Sr is the best size to get a cubic space group $Fm\bar{3}m$ structure with close tolerance factor 1. In general, the size of A ion influences the crystal symmetry significantly while that of the B ion does not change the symmetry, but changes the lattice volume proportionally [28,29]. Unfortunately, theoretical report has not keep pace with it. In our previous work [30], we gave the prediction of ferromagnetism induced by Al vacancy or Ta vacancy in SAT. As a part of integrated work on possible ferromagnetism induced by point-defects, especially by nonmagnetic elements doping at B sites in SAT, we think that a first-principles investigation is required and interesting. So we will focus our attention on B-site substitution in SAT by Cu or Zn aiming at investigating the possible ferromagnetism in this paper.

2. Computational methods

We carry out first-principles calculations based on the density functional theory (DFT). In particular, we use the pseudopotential method as implemented in the SIESTA code [31–33], which is a fully self-consistent DFT method based on a linear combination of atomic orbitals (LCAO) basis set with linear scaling. Meanwhile, we use the double- ξ plus polarization (DZP) basis set, which has been shown to yield high-quality results for most of the systems studied. Normconserving pseudopotentials for Cu, Zn, O, Al, Sr and Ta are generated using the Troullier Martins method [34] within the generalized gradient approximation (GGA) [35], as established on the parametrization scheme of Perdew-Burke-Ernzerhof (PBE). Brillouin zone sampling is carried out with a $8 \times 8 \times 8$ Monkhorst-Pack grid and a mesh cutoff of 300 Ry is used. The spin polarized and spin unpolarized calculations are performed in all cases. The system is modeled with 40-atom unit cell (space group $Fm\bar{3}m$, No. 225) in which the component atoms occupied the following positions: Sr (0.25,0.25,0.25), Al (0,0,0), Ta (0.5,0.5,0.5), and O (0.25,0,0). To construct a B-site doped system, one Al atom or Ta atom was substituted by one Cu or Zn atom, denoted as Cu_{Al} , Zn_{Al} , Cu_{Ta} and Zn_{Ta} , respectively. The conjugate gradient algorithm is adopted and all the geometries were optimized until the residual forces reached values less than 0.01 eV/Å. Also, total energy convergence criterion of 10^{-4} eV is used.

3. Results and discussions

As a preliminary step, we checked the reliability of this strategy by verifying the good reproduction of the structural properties for undoped SAT as did in our previous paper [30]. Especially, the relaxed lengths of Sr—O bond, Al—O bond and Ta—O bond are 2.7764 Å, 1.9334 Å and 1.9928 Å, respectively, which are consistent well with the experimental results of 2.7538 Å, 1.8987 Å and 1.9953 Å, respectively [27]. For the case of B-site doped SAT, the supercell structures are also predicted to be stable in the cubic symmetry with space group $Fm\bar{3}m$. Both the direction of lattice vectors and the relative atomic coordinations have hardly changed except for the lattice parameters and the coordinations of O atoms near the dopants after the relaxation process, as that of metals (Al, Nb, Cu, Zn etc)-doped cubic $BaTiO_3$ [36]. The relaxation results are listed in Table 1. Both the optimized lattice constants ($a(\text{Å})$) and the distances between the dopants and the neighboring O atoms after the structure relaxation of doped SAT are enlarged slightly, although smaller changes appear for the formers. Take Cu_{Al} in SAT as an example, the optimized lattice constant and the Cu—O bond length are enlarged from 7.8523 Å, 1.9334 Å to 7.8885 Å, 2.0341 Å, an increase less than 0.47%, 5.21%, respectively. This may related to the bigger ionic radius and larger electronegativity of the dopants compared with the substituted hosts.

Theoretically, it is important to predict whether the doped impurity is stable or not. The formation energy of a single Cu (or Zn) impurity E_{form} can be written as $E_{form} = E_{doped} - E_{pristine} + (\mu_X - \mu_M)$, where $E_{pristine}$ and E_{doped} are the total energies of the perfect supercell and the

Table 1

The optimized lattice constant $a(\text{Å})$, the distances change $\Delta d(\text{Å})$ of the first nearest-neighboring O atoms around the dopant after and before the structure relaxation in SAT, the calculated defect formation energy $E_{form}(\text{eV})$, the energy difference $\Delta E_{FN}(\text{meV})$ between the ferromagnetic state E_{FM} and the nonmagnetic state E_{NM} , the energy difference $\Delta E_{FA}(\text{meV})$ between the ferromagnetic state E_{FM} and the anti-ferromagnetic state E_{AFM} , and the magnetic moment $MM(\mu_B)$ of spin-polarized state for SAT with dopants.

	Cu_{Al}	Zn_{Al}	Cu_{Ta}	Zn_{Ta}
a	7.8885	7.9112	7.8487	7.8779
Δd	0.1007	0.1237	0.0796	0.1355
E_{form}	7.4202	6.0826	11.9196	10.8414
ΔE_{FN}	0.103	0.742	−464.968	−35.566
ΔE_{FA}	—	—	−13.31	−35.214
MM	0.000797	0	3.9057	2.87908

doped supercell, respectively. μ_X and μ_M are the chemical potentials of X(=Al, Ta), and M(Cu, Zn), respectively. The chemical potentials determine the off stoichiometry of the system, which depends on the material grown conditions and satisfies boundary conditions. Here, μ_X and μ_M are taken as the energies of the single atom of Al, Ta and Cu, Zn in their bulk. μ_{Cu} and μ_{Al} are calculated from face-centered cubic Cu and Al, μ_{Ta} from body-centered cubic Ta, μ_{Zn} from hexagonal zinc(Zn), respectively. The calculated formation energies E_{form} are also listed in Table 1. The smaller value of the formation energy means the greater stability of the structure. Generally, the substitution at Al-site is more easier than at Ta-site and the most energetically stable one is Zn_{Al} , E_{form} being the smallest 6.0826 eV.

Towards the stability of ferromagnetism the total energy difference (spin-polarization energy) between the ferromagnetic states (FM) and nonmagnetic (NM) states ($\Delta E_{FN} = E_{FM} - E_{NM}$) was calculated and given in Table 1. When $\Delta E_{FN} < 0$ the ferromagnetic states are more stable than nonmagnetic states, and vice versa. It can be seen that for Al-site substitutions the nonmagnetic states are more stable but for Ta-site substitutions the ferromagnetic states have the lower energies. The energies of ferromagnetic states for Cu_{Ta} and Zn_{Ta} favor over the energies of nonmagnetic states by 464.968 meV, 35.566 meV and also reveal a total magnetic moment of 3.91 μ_B /supercell, 2.88 μ_B /supercell. To examine the type of magnetic coupling between the two dopants we constructed a $1 \times 1 \times 2$ supercell containing 80 atoms for each of Cu_{Ta} and Zn_{Ta} . Two Cu (or Zn) atoms are put in the same substituted Ta-site, and therefore possessing the same defect concentration as in the previous unit cells. Both the energies of ferromagnetic and anti-ferromagnetic states for the doped system are calculated with a $8 \times 8 \times 4$ k-point mesh. A magnetization energy is defined as $\Delta E_{FA} = E_{FM} - E_{AFM}$, where E_{FM} and E_{AFM} represent the total energy of the doped system in ferromagnetic and anti-ferromagnetic states, respectively. A negative value means the ferromagnetic state is more stable. As listed in Table 1, The energies of ferromagnetic states for Cu_{Ta} and Zn_{Ta} are lower than the energies of anti-ferromagnetic states 13.31 meV, 35.21 meV, respectively. And hence the ferromagnetism can be expected in SAT doped with Cu (or Zn) at Ta-site.

After the geometric, energetic and magnetic investigations on the B-site doped SAT, the density of states and the spin charge density will be used to give insights into the origin of the ferromagnetism driven by nonmagnetic dopants (Cu, Zn) at Ta-site.

The calculated total density of states(DOS) for Cu_{Ta} in SAT is plotted in Fig. 1(a). Both the majority spin bands and the minority spin DOS cross the Fermi level and exhibit a metallic-like semiconductor character. More obviously, hole states, i.e., the minority spin states, emerge at 0.97eV above Fermi level in the energy band gap, which are mostly from CuO_6 octahedron. The local magnetic moment may originate from the combination of Hund's rule and crystal field effect. As we know in perfect SAT, each Ta atom is surrounded by six O atoms forming TaO_6 octahedron. The Ta 4d states are split into the twofold

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