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Gd-doping-induced insulator-metal transition in $SrTiO_3$

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ABSTRACT

Recently, insulator-metal transition was found experimentally in Gd-doped $SrTiO_3$ films. Here, we present first-principle investigation on the structural, electronic and magnetic properties of $Sr_{1-x}Gd_xTiO_3$ within density-function theory. The spin-polarized calculations give a diamagnetic insulator at x=0, a ferrimagnetic metal $0.125 \le x \le 0.5$ and a ferrimagnetic insulator x=1 and all Ti ions moments are antiparallel to Gd ions moments. Magnetic Gd-doping distorts the structures of $Sr_{1-x}Gd_xTiO_3$ films and results in ferrimagnetism. Doped electrons occupy the bottom of conduction bands so that insulator-metal transition occurs. These calculated results are in agreement with available experiments.

1. Introduction

$SrTiO_3$ is a band insulator, which has a 3.2 eV band gap [1]. It is used widely as thermoelectric devices [2], memory devices [3] and piezoelectric devices [4]. And it has attracted extensive attention owing to many fascinating phenomena it displayed such as ferromagnetism [5], superconductivity [6], structure phase transition [7], two-dimensional electron gas [8], etc.

Conductor electrons were drawn into $SrTiO_3$ when transition-metal oxides were grown on $SrTiO_3$ such as $LaAlO_3/SrTiO_3$ superlattices [9,10]. Additionally, conductor electrons in $SrTiO_3$ can be induced by oxygen vacancy [11] and substitutional rare-earth ions doping [12–17]. $SrTiO_3$ with oxygen vacancy underwent insulator-metal transition [11], which was tempted by the carrier freeze-out effect. Partial substitution in Sr sites with La atoms in $SrTiO_3$ generated a strongly correlated metal phase [17]. The optically doped $SrTi_{1-x}Nb_xO_3$ was identified as a multi-band s-wave superconductor [12]. Cr doping in $SrTiO_3$ resulted in insulator-metal transition [18]. Recently, insulator-metal transition also occurred in Gd-doped $SrTiO_3$ or Sr-doped $GdTiO_3$ and a ferrimagnetic metal phase was found [16]. Due to the characteristic of insulator-metal transition in doped $SrTiO_3$, $SrTiO_3$ has promising applications such as memory device, etc. This makes it important to understand theoretically the nature of insulator-metal transition in doped $SrTiO_3$.

In order to understand the experimentally-observed insulator-metal transition and ferrimagnetism in Gd-doped $SrTiO_3$ films [16], we made first-principle calculations on the structural, electronic and magnetic properties of $Sr_{1-x}Gd_xTiO_3$ within density-function theory (DFT) based on generalized gradient approximation plus U (GGA + U). The present theoretical results match with available experimental evidence. We interpret well the phenomenon of insulator-metal transition in $Sr_{1-x}Gd_xTiO_3$ and reveal the origin of ferrimagnetism.

2. Calculation detail

The first-principle calculations of $Sr_{1-x}Gd_xTiO_3$ (x=0, 0.125, 0.25, 0. 5 and 1) were performed within DFT based on a projector-augmented wave (PAW) [19] potentials as implemented in Vienna ab-inito simulation package (VASP) [20]. For the exchange-correlation functions, we used GGA+U with the Perdew-Burke-Ernzerhof (PBE) scheme. All calculations were performed with the Hubbard U=5.0 and an approximation of the Stoner exchange parameter J=0.64 applied on d-orbitals of Ti atoms [21]. First, bulk $SrTiO_3$ and $GdTiO_3$ were fully relaxed. A 40-atom $SrTiO_3$ supercell with size 2×2×2 and a 20-atom $GdTiO_3$ unit cell were used for calculations. Next, $Sr_{1-x}Gd_xTiO_3$ ($0 < x \le 0.5$) films were fully optimized. A few of Sr atoms in $SrTiO_3$ supercell were substituted by Gd atoms to calculate $Sr_{1-x}Gd_xTiO_3$ films. In order to reproduce experiment results [16], the parameters in ab plane were fixed as 7.810 Å, two times of the experimental lattice parameter of $SrTiO_3$ substrate [22]. The lattice parameter along c axis and all atom positions were fully optimized in $Sr_{1-x}Gd_xTiO_3$ ($0 < x \le 0.5$) films. The plane-wave energy cutoff for the electrons was 400 eV. A 5×5×5 grid of Monkhorst–Pack mesh was used for the k-point sampling in $Sr_{1-x}Gd_xTiO_3$ ($0 \le x \le 0.5$) and A 8×8×6 grid in $GdTiO_3$. Six electrons ($2s^22p^4$), ten electrons ($4s^24p^65d^2$), four electrons ($3d^34s^1$) and eighteen electrons $4d^75^25p^65d^16s^2$, treated as valence electrons, were for

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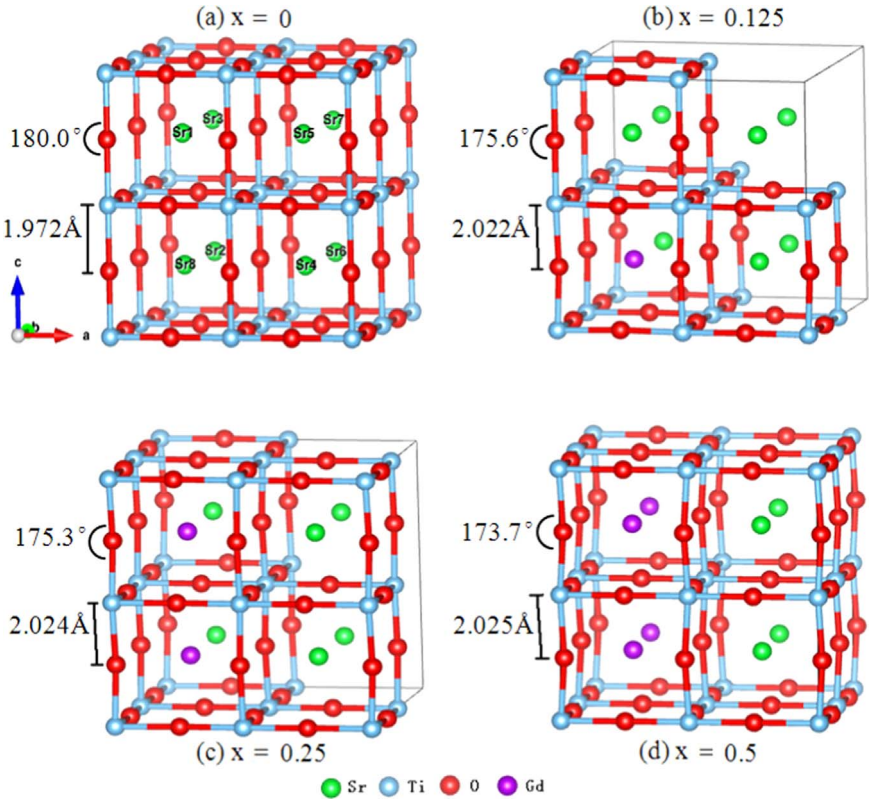

Fig. 1. (Color online) Optimized structures of bulk $SrTiO_3$ (x=0) and $Sr_{1-x}Gd_xTiO_3$ films (0 < x≤0.5): (a) x=0, (b) x=0.125, (c) x=0.25 and (d) x=0.5.

Table 1
The lattice parameters, band gaps and magnetic ground states of $SrTiO_3$ and $GdTiO_3$.

	$SrTiO_3$		$GdTiO_3$work	
	Experiment	This work	Experiment	This work
a(Å)	3.905[22]	3.945	5.403[23]	5.437
b(Å)	3.905	3.945	5.701	5.782
c(Å)	3.905	3.945	7.674	7.737
band gap(eV)	3.22[1]	2.35	> 0[26]	1.90
the magnetic ground state	diamagnetic[24]	diamagnetic	ferrimagnetic[25]	ferrimagnetic

Table 2
Magnetic moment at atom sites in the ground state of bulk $SrTiO_3$ and $Sr_{1-x}Gd_xTiO_3$ films.

$Sr_{1-x}Gd_xTiO_3$	Atom sites	magnetic moments (μ_B)
x=0	Ti	0
x=0.125	Ti	−0.036
	Gd	6.801
x=0.25	Ti	−0.246
	Gd	6.785
x=0.5	Ti	−0.446
	Gd	6.747
x=1	Ti	−0.958
	Gd	6.897

the O, Sr, Ti and Gd atoms, respectively. Between successive iterations the electronic calculations were converged to 10^{-5} eV, and the Hellman-Feynman force calculations were converged to less than 10^{-4} eV/Å.

3. Results and discussion

3.1. Structure relaxation and magnetic properties

First, the structures of bulk $SrTiO_3$ and $GdTiO_3$ were optimized. $SrTiO_3$ is a typical cubic structure with Pm-3m space group [22] while $GdTiO_3$ has a highly distorted perovskite structure with Pbnm space group [23]. The experimental lattice parameter a=3.905 Å is for $SrTiO_3$ [22] and a=5.403, b=5.701, and c=7.674 [23] are for $GdTiO_3$. As shown in Fig. 1(a), TiO_6 octahedral has a cubical structure where Ti atom is at the center and O atoms are at the ends of the edges. The parameters a, b and c, the ground states and band gaps are listed in Table 1. The calculated lattice parameters of a=3.945 Å for $SrTiO_3$ and a=5.437 Å, b=5.782 Å and c=7.737 Å for $GdTiO_3$ are in reasonable accordance with the previous experimental values [22,23]. The ground states of $SrTiO_3$ and $GdTiO_3$ are diamagnetic and ferrimagnetic insulators, respectively, in agreement with experimental results [1,24–26]. The total energy of A, G and C-type antiferromagnetic configuration of $GdTiO_3$ are higher than the ferrimagnetic structure by 0.05, 0.81 and 0.82 eV per formula. Ferromagnetic $GdTiO_3$ converges to ferrimagnetic state, where all Ti ions moments are antiparallel to those of Gd ions. As shown in Table 2, the calculated magnetic moments in $GdTiO_3$ are $-0.958\mu_B$/Ti and $6.897\mu_B$/Gd.

Second, $Sr_{1-x}Gd_xTiO_3$ films (x=0.125, 0.25 and 0.5) were calculated. The present calculated results show that the ground states of the $Sr_{1-x}Gd_xTiO_3$ films are ferrimagnetic, where all moments of Ti ions are antiparallel to those of Gd ions. In order to reproduce experimental results [16], the parameters within the ab plane were fixed as 7.810 Å, namely, two times of the experimental lattice parameter a of $SrTiO_3$ substrate. Then the lattice parameter along c axis and all atom positions are fully optimized. All optimized structures of the ground states in $Sr_{1-x}Gd_xTiO_3$ films (x=0.125, 0.25 and 0.5) are shown in Fig. 1. Green, blue, red and purple spheres represent Sr, Ti, O and Gd atoms, respectively. Three different types [27] of structures were modeled for $Sr_{0.75}Gd_{0.25}TiO_3$, which were constructed by substituting