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Vacancy induced magnetism in $SrTiO_3$

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ABSTRACT

Vacancy-induced magnetism in perovskite $SrTiO_3$ is investigated by *ab initio* calculations and magnetic measurements. The calculations of the generalized gradient approximation (GGA), the local density approximation (LDA) and the local density approximation with on-site effect U (LDA+U) methods show that stoichiometric $SrTiO_3$ is nonmagnetic. The GGA calculated results indicate that Ti or O vacancy could induce magnetism rather than Sr vacancy. The LDA and LDA+U calculations show that the Ti vacancy could induce magnetism, while Sr and O vacancies couldn't. The experimental results confirm that $SrTiO_3$ nanocrystalline powders exhibit room-temperature ferromagnetism (FM) and the magnetic moment results from cation vacancies.

1. Introduction

Room temperature ferromagnetism (FM) in pure semiconductors or insulators without any ferromagnetism elements has attracted much attention in recent years. The experimental results had indicated that observed FM originate from the oxygen vacancies for HfO_2, CeO_2, Al_2O_3, ZnO, In_2O_3, SnO_2 and TiO_2 films/nanograins [1–5], but from neutral cation vacancies for MgO films/nanograins [6–9]. Most of *ab initio* calculations had demonstrated that neutral cation vacancies are responsible for the magnetic moment in oxides such as TiO_2, ZnO, SnO_2, ZrO_2 and MgO [10–19]. It is interesting to find that nanocrystalline $BaTiO_3$ [20], $La_2Ti_2O_7$ [21] and $PbTiO_3$ [22] plates and $(K_{0.5}Na_{0.5})NbO_3$ films [23] can exhibit multiferroic properties, showing the simultaneous occurrence of ferromagnetism (FM) and ferroelectricity (FE). $BaTiO_3$, $La_2Ti_2O_7$, $PbTiO_3$ and $(K_{0.5}Na_{0.5})NbO_3$ bulks are traditional ferroelectric perovskite materials, and their sintered bulks at high temperature are nonmagnetic. The *ab initio* calculation by Mangalam et al. [20] with LDA method indicated that FM in $BaTiO_3$ originates from the oxygen vacancy. However, *Ab initio* calculations by Cao et al. [24] with GGA method showed that both cation (Ti) vacancies and anion (O) vacancies could induce magnetism in $BaTiO_3$. Experimental results indicate that the observed FM originates from oxygen vacancies in $La_2Ti_2O_7$ and $PbTiO_3$ nanocrystalline plate [21,22], but the FM in $(K_{0.5}Na_{0.5})NbO_3$ nanocrystalline films comes from (K, Na) cation vacancies [23].

Conventional bulk $SrTiO_3$ with cubic structure is incipient ferroelectrics, or quantum paraelectrics, which is of great interest due to their high dielectric constant, low dielectric losses and high degree of tenability by the applied electric field and temperature [25–27]. It has been recently demonstrated that the strained $SrTiO_3$ films [28,29] and nanocrystalline plates [30] with pseudo-cubic structure could exhibit ferroelectricity even at room temperature. It evokes our interest to look for the possibility of ferromagnetism in $SrTiO_3$. Recently, Shein et al. and Adeagbo et al. have studied the magnetism of perovskite $SrTiO_3$ bulk and (100) surface using WIEN2k package and Vienna ab initio simulation package (VASP) by the generalized gradient approximation (GGA) method, respectively, and found that the Ti and O vacancies could induce magnetism, nevertheless, the Sr vacancy cannot induce magnetism [31,32]. Eliseev et al. also considered that O vacancy can produce magnetism in $SrTiO_3$ [33]. Djermouni et al. performed a detailed investigation of the structural and electronic properties of single and double oxygen vacancy defects in bulk $SrTiO_3$ and found that the introduction of oxygen vacancies in $SrTiO_3$ decreased the lattice constants and bulk module [34]. In addition, Potzger et al. found that defect can induce ferromagnetism in crystalline $SrTiO_3$ by experiments [35]. In our present work, with the help of *ab initio* calculations and magnetic measurements, the possibilities of vacancy-induced magnetism in perovskite $SrTiO_3$ are investigated. Our GGA calculations show that Ti and O vacancies could induce the ferromagnetism. Whereas, the LDA and LDA+U calculations indicate that only Ti vacancy can introduce the ferromagnetism in $SrTiO_3$. The experimental results also show that $SrTiO_3$ nanocrystalline powders could exhibit room-temperature ferromagnetism. The vacuum heat-treatment greatly reduces the

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FM of $SrTiO_3$ nanocrystalline powders, which implies that it is cation vacancies rather than oxygen vacancies that introduce the FM in $SrTiO_3$.

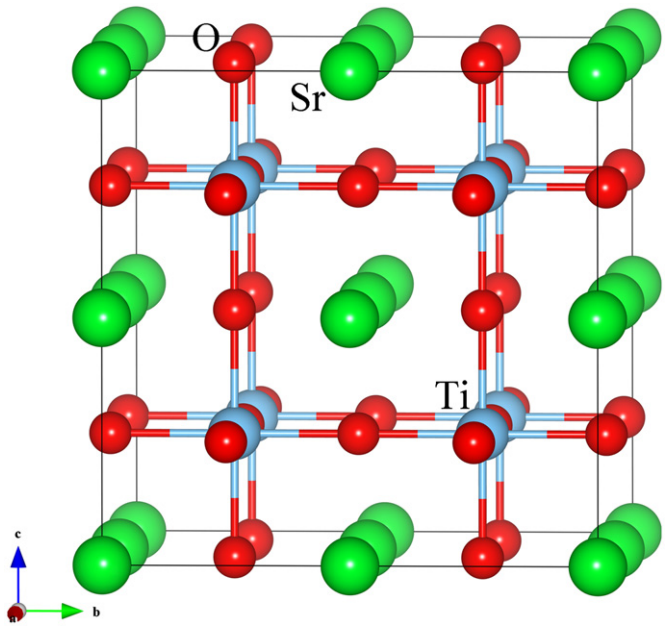

Fig. 1. Crystal structural of cubic $SrTiO_3$. Green balls, blue balls, and red balls represent Sr atoms, Ti atoms, and O atoms, respectively.

2. Computational methods

The density functional theory (DFT) calculations were performed using the plane-wave pseudopotential method in the Vienna ab initio simulation package (VASP) [36,37]. The projector augmented wave (PAW) [38,39] potentials were employed. The GGA as well as LDA schemes were used to describe the exchange correlation energy. Considering the fact that LDA may underestimate the Coulomb repulsion and tend to overlocolize the charge density, strong correlation effects were introduced by means of the LDA+U [38] scheme. In our LDA+U calculation, the on-site effective parameter U_{eff} ($=U-J$) was chosen as 5.8 eV for Ti atom. A $2\times2\times2$ supercell containing 40 atoms was relaxed to get the most stable structure of cubic $SrTiO_3$ with group of Pm3m (see Fig. 1). The calculated lattice constants of ($a=b=c=3.9$ Å and $\alpha=\beta=\gamma=90^\circ$) were in good agreement with our experimental results. Special k points were generated with a $3\times3\times3$ grid based on Monkhorst-Pack scheme. The cases of stoichiometric $SrTiO_3$ and nonstoichiometric $SrTiO_3$ with Sr, Ti and O vacancies were considered, respectively. The total energy was converged to be 1.0×10^{-4} eV/atom, while the Hellman-Feynman force was smaller than 0.01 eV/Å in the optimized structure.

3. Experiments

$SrTiO_3$ nanocrystalline powders were prepared by sol-gel method. 0.2 mol $Sr(NO_3)_2\bullet4\,H_2O$ with a purity of 99.99 wt%

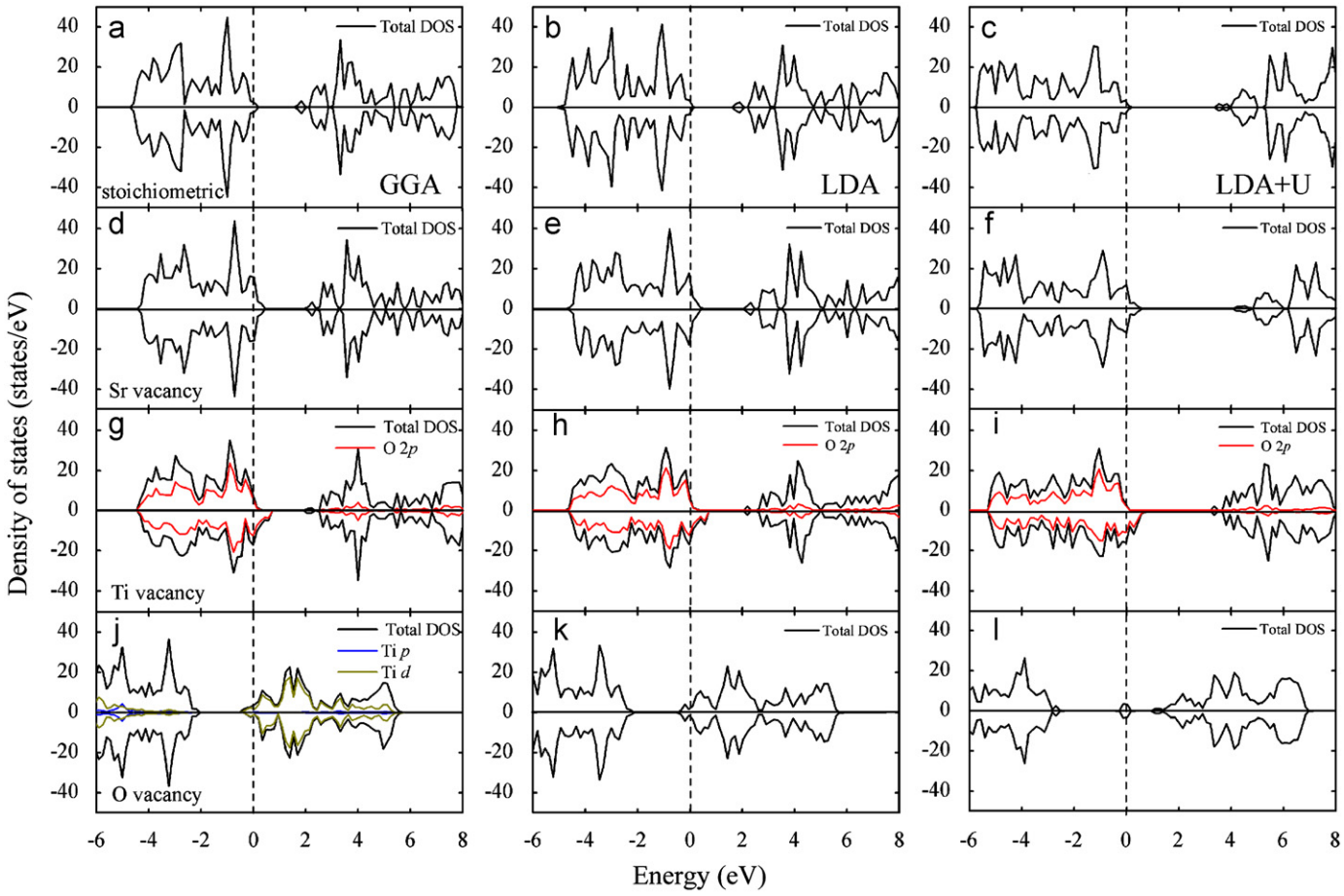

Fig. 2. Spin resolved total DOSs for (a)-(c) stoichiometric cubic $SrTiO_3$; (d)-(f) cubic $SrTiO_3$ with one Sr vacancy; (g)-(i) cubic $SrTiO_3$ with one Ti vacancy; (j)-(l) cubic $SrTiO_3$ with one O vacancy. The vertical dotted line indicates the Fermi level.