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Magnetism without magnetic ions in non-magnetic perovskites $SrTiO_3$, $SrZrO_3$ and $SrSnO_3$

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Abstract

Using the full-potential linearized augmented plane-wave (FP-LAPW) method with the generalized gradient approximation (GGA) for the exchange-correlation potential, we studied spin polarization induced by replacement of oxygen atoms by non-magnetic 2p impurities (B, C and N) in non-magnetic cubic $SrMO_3$ perovskites, where M = Ti, Zr and Sn. The results show that the magnetization may appear because of the spin–split impurity bands inside the energy gap of the insulating $SrMO_3$ matrix. Large magnetic moments are found for the impurity centers. Smaller magnetic moments are induced on the oxygen atoms around impurities. It is shown that $SrTiO_3$:C and $SrSnO_3$:C should be magnetic semiconductors while other compounds in this series ($SrTiO_3$:B, $SrTiO_3$:N and $SrZrO_3$:C) are expected to exhibit magnetic half-metallic or pseudo-half-metallic properties.

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1. Introduction

Perovskite-like oxides attract attention owing to their interesting magnetic, electronic and transport properties. For instance, the perovskites are often used as a base to develop materials for spin- and opto-electronics [1–4]. Particular efforts, both theoretical and experimental, have been undertaken for the design of perovskite-based magnetic half-metals (MHMs). The desired MHM behavior for the cubic perovskites AMO_3 (where A represents a lanthanide or an alkali-earth metal and M is a transition metal) may be achieved by substituting

- (i) non-magnetic A ions with other non-magnetic ions [5],
- (ii) magnetic M ions with other magnetic ions [6–8],
- (iii) magnetic M ions with non-magnetic ions [9], or
- (iv) by combining the doping strategies (i)–(iii) [10].

The formation of the MHM state in these doped systems depends on a quite complicated combination of super-exchange interactions and pd_σ–pd_π hybridization of d metal and oxygen ions [5–10]. It should be emphasized that most of the known perovskite-like MHMs contain magnetic d atoms with open d^n shells ($1 \leqslant n \leqslant 9$).

On the other hand, very recently much attention has been attracted to the discovery of magnetism in the series of non-magnetic simple oxides (e.g. MgO [11–13], CaO [12,14–16], ZnO [17], TiO_2 [18–20], BeO [21] and some others [4,22]), where it is caused by the presence of structural vacancies or non-magnetic sp impurities. However, similar phenomena in more complicated ternary oxides are not known at present.

In this work, we have focused on the possibility of the spontaneous magnetization for non-magnetic perovskites induced by non-magnetic sp impurities. For this purpose by means of the *ab initio* band structure calculations, we analyze the doping effects on the electronic and magnetic properties of series of insulating perovskites $SrMO_3$, where

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M are Ti, Zr and Sn, caused by the 2p impurities—nitrogen, carbon and boron—in assumption that these impurity atoms would replace the oxygen atoms in $SrMO_3$.

Note that some available experimental data testify the existence of such systems and allow us to make such assumption. For example, strontium titanate thin films with relatively high nitrogen concentration were prepared [23,24] and for nitrogen-doped films their thermal stability has been confirmed [25]; these results indicate the possibility of substitutional doping for nitrogen into the $SrTiO_3$ lattice. Besides, some other evidences of the presence of substitutional nitrogen (or carbon) inside various strontium titanate nano-scale species are also reported [26–28]. On the other hand, any data on the presence of boron impurity in $SrMO_3$ are unknown, so the systems $SrMO_3$:B were considered as the additional model examples.

Thus, the chosen systems allow us to discuss the magnetization effects for the series of insulating perovskites $SrMO_3$ in the presence of substitutional 2p impurities depending

(i) on the type of 2p dopants—on example of the same matrix: $SrTiO_3$ doped with boron, carbon or nitrogen, and
(ii) on the type of perovskite matrix—on example of $SrTiO_3$, $SrZrO_3$ and $SrSnO_3$ doped with the same impurity—carbon.

We have found that a spontaneous spin polarization of the 2p impurity states arises in $SrMO_3$ matrix and the impurity ions acquire significant magnetic moments (MMs). Moreover, the localized magnetic moments (relatively small) are induced on the oxygen atoms around the impurity ions.

2. Models and method

The $SrMO_3$ perovskites under consideration crystallize with cubic structure (space group; Pm3m) where atomic positions in the elementary cell are M: 1a (0, 0, 0); O: 3d (0, 0, 1/2); and Sr: 1b (1/2, 1/2, 1/2). Our model of doping mechanism assumes that the selected 2p impurities (X = B, C or N) replace the oxygen centers in $SrMO_3$ perovskites, and this situation is described by substituting the oxygen atom in the 40-atomic supercell with an impurity atom X. The supercell symmetry is tetragonal, space group is P4/mmm. The composition of the doped systems corresponds to the formula $SrMO_{2.875}X_{0.125}$.

The calculations have been performed using the Vienna package WIEN2k, which is an implementation of the hybrid full-potential (linearized) augmented plane-wave plus local orbitals (FP-LAPW + lo) method within the density-functional theory [29]. The electronic configurations are taken [Ar] $3d^24s^2$ for Ti, [Kr] $4d^25s^2$ for Zr, [Kr] $4d^{10}5s^25p^2$ for Sn, [Kr] $5s^2$ for Sr and [He] $2s^22p^4$ for O. The electronic configurations of impurity atoms are [He] $2s^22p^1$ for B, [He] $2s^22p^2$ for C and [He] $2s^22p^3$ for N. Here, the noble gas core states are distinguished from the subshells of valence electrons. The basis set inside each MT sphere is split into core and valence subsets. The core states are treated within the spherical part of the potential only, and are assumed to have spherically symmetric charge distribution confined within MT spheres. The valence part is treated with the potential expanded into spherical harmonics up to $l = 4$. The valence wave functions inside the spheres are expanded into spherical harmonics up to $l = 10$. The plane-wave expansion takes place with $R_{MT} \times k_{max}$ equal to 7.0, and k sampling with $5 \times 5 \times 5$ k-points mesh in the Brillouin zone is used. All calculations are carried out with optimized lattice constants. We used the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) [30] for the exchange-correlation potentials. Relativistic effects are taken into account within the scalar-relativistic approximation. Due to the periodic boundary condition, our calculations are performed in a ferromagnetic ordering configuration.

The self-consistent calculations are supposed to have converged when the difference in the total energy of the system did not exceed 0.1 mRy as calculated at consecutive steps. We have adopted the MT radii of 2.5 a.u. for Sr, 1.87 a.u. for Ti, 1.98 a.u. for Zr and 1.83 a.u. for Sn. The MT radii for O and for the substituting 2p atoms are adopted as 1.65, 1.75 and 1.83 a.u. in $SrTiO_3$, $SrZrO_3$ and $SrSnO_3$ compounds, respectively. The total density of states (DOS) is obtained by making use of a modified tetrahedron method [31].

3. Results and discussion

3.1. Electronic properties of non-magnetic perovskites $SrTiO_3$, $SrZrO_3$ and $SrSnO_3$

At the first stage, the ground state properties and band structures of the ideal non-magnetic perovskites $SrMO_3$ are calculated. The main results and their comparison with some available experimental and theoretical data are shown in Table 1. As can be seen, the obtained lattice constants a_0 are very close to experimental data; the deviations achieve only about 1–2%. Other important ground state parameters, bulk modules B, also agree well with the available data.

The elementary cell parameter is found to increase as $a_0(SrTiO_3) < a_0(SrSnO_3) < a_0(SrZrO_3)$, and this result can be explained as reflecting respective increase in the ionic radii of M-atoms, namely $R(Ti) = 0.605\,Å < R(Sn) = 0.69\,Å < R(Zr) = 0.72\,Å$. The bulk modules are found to decrease as $B(SrTiO_3) > B(SrSnO_3) > B(SrZrO_3)$, i.e. inverse to a_0, which is in agreement with the well-known relationship between B and lattice constants [43]. This simple trend has also been demonstrated for a number of other perovskites [34].

The total and l-projected DOS for the equilibrium geometry of the perovskites under study are shown in