Local Symmetry Breaking for Negatively Charged Impurity Centers in \( \text{SrTi}_{1-x}\text{Mn}_x\text{O}_3 \)

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Abstract—First-principles calculations of the geometry and electronic structure of the impurity center in \( \text{SrTi}_{1-x}\text{Mn}_x\text{O}_3 \) have been performed. Neutral and negatively charged defects are considered. It is found that the doubly charged impurity center is polar; it has \( C_{4v} \) symmetry and electronic state \( ^4B_1 \) with electron polaron localized at one of the neighboring titanium atoms. It is shown that this state is due to the spontaneous breaking of the defect local symmetry: \( O_h(4A_{1g}) \rightarrow D_{4h}(4B_{1g}) \rightarrow C_{4v}(4B_1) \).

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INTRODUCTION

Ferroelectrics with perovskite structures have unique physicochemical properties and, therefore, are very promising for microelectronic devices. The presence of impurity atoms, as well as a deviation from stoichiometry (even in nominally pure materials), may substantially affect the electric (dielectric parameters and conductivity), magnetic, optical, mechanical, and other properties of ferroelectrics. At the same time, the problem of deliberately changing the properties of materials is very important. One way of technological engineering is the formation of structural defects (intrinsic, radiation, and produced by impurity atoms), which can affect certain properties of materials in fairly wide ranges. There is much interest in the point defects in \( \text{SrTiO}_3 \) doped with Mn and Cr. Strontium titanate is a model material of the perovskite family \([1, 2]\). Dielectric relaxation was revealed in \( \text{SrTiO}_3: \text{Mn} \) \([3–7]\), the nature of which remains unclear \([8, 9]\). Kleemann et al. \([10]\) established that phases of polar and spin glasses coexist in ceramic \( \text{Sr}_{0.98}\text{Mn}_{0.02}\text{TiO}_3 \) samples and observed the magneto-electric effect in them. Finally, chromium-doped \( \text{SrTiO}_3 \) is a promising material for resistive memory devices \([11–13]\).

When studying doped materials, it is important to analyze the structure of specific defects and primarily perform a theoretical simulation of defects using first-principles calculations. Recently, first-principles calculations of the electronic structure have been performed for oxygen vacancies in strontium titanate \([14–17]\) and for point defects generated by substitutional donor and acceptor impurities in the \( B \) position (V and Sc \([14]\), Fe \([18]\), Mg \([8]\), and Mn \([8, 9]\)) and in the \( A \) position (Mg, Zn, Ca, Ba, Pb \([19, 20, 8, 9]\), and Mn \([8, 9, 21]\)). In this paper, we report the results of first-principles calculations of the electronic structure and geometry of the isolated point defect related to the substitution of titanium with manganese in the \( B \) position in \( \text{SrTiO}_3 \). The structure of the polaron ground state in the doubly charged defect and spontaneous breaking of local symmetry, which is caused by the defect transition from the nonpolar state with the \( D_{4h} \) symmetry (electronic state \( ^4B_{1g} \)) to the polar state with the \( C_{4v} \) symmetry (electronic state \( ^4B_1 \)), is investigated.

CALCULATION METHODS

Point defect is the simplest object that violates periodicity and forms disorder in crystal. There are two alternative approaches to \( \text{ab initio} \) calculations of point defects. The supercell method, which considers a periodic structure with a defect-containing primitive cell whose volume exceeds that of the initial primitive cell several times, is generally used. Actually, this approach deals with a new compound, the spatial symmetry of which may differ from the matrix symmetry. A more adequate method is the cluster approach, where the crystalline environment of the defect is modeled by a quasi-molecular cluster of appropriate symmetry passivated by hydrogen atoms with frozen initial positions \([8, 19]\). This makes it possible, on the one hand, to saturate dangling oxygen—transition metal bonds and significantly reduce the cluster charge. At the same time, the fixation of hydrogen atoms during geometry optimization (the search for equilibrium geometry) makes it possible to imitate the asymptotic boundary conditions of zero forces and strains at large distances from a single defect in a crystal. A seven-octahedra \( \text{MnO}_6\text{Ti}_6\text{Sr}_8(\text{OH})_{30} \) cluster was...
defect: carriers. Here we consider three charged states of the presence of distant donor centers or photoactivated pure material) or charged states, for example, in the defect can be in either neutral (at least in nominally covalently coordinated by oxygen atoms. In this case, the spin–orbit interaction was disregarded.

The electronic problem was solved within the density-functional theory with the B3LYP hybrid functional method from the quantum-chemical GAUSSIAN 03 program package [25]. The calculation details (choice of atomic bases, etc.) were reported in [8, 19]. The calculation results are listed in Tables 1 and 2.

Table 1. Symmetry and total energy of the Mn defect in the B position in SrTiO$_3$ (the replacement of the Ti atom) for three charge states of the defect ($Z_d$) and different spin multiplicities ($2S + 1$)

| $Z_d = 0$ |
|---|---|---|---|---|
| $2S + 1$ | 2 | 4 | 6 | 8 |
| Point symmetry of the defect | $D_{2h}$ | $O_h$ | $D_{2h}$ | $D_{4h}(s)$ |
| Electronic state of the defect | $^2B_{2g}$ | $^4A_{1g}$ | $^6B_{3g}$ | $^8A_{2g}$ |
| Total energy (in atomic units) | $-8981.66521$ | $-8981.73665$ | $-8981.65687$ | $-8981.55987$ |
| Energy loss (eV) | 1.94 | 0 | 2.17 | 4.82 |

| $Z_d = -1$ |
|---|---|---|---|---|
| $2S + 1$ | 1 | 3 | 5 | 7 |
| Point symmetry of the defect | $D_{4h}(s)$ | $D_{4h}(s)$ | $D_{4h}(e)$ | $D_{4h}(e)$ |
| Electronic state of the defect | $^1A_{1g}$ | $^3A_{3g}$ | $^1B_{2g}$ | $^1A_{1g}$ |
| Total energy (in atomic units) | $-8981.96176$ | $-8981.97954$ | $-8982.00065$ | $-8981.90708$ |
| Energy loss (eV) | 1.06 | 0.57 | 0 | 2.55 |

| $Z_d = -2$ |
|---|---|---|---|---|
| $2S + 1$ | 2 | 4 | 6 |
| Point symmetry of the defect | $D_{2h}$ | $D_{4h}(s)$ | $C_{4v}$ | $O_h$ |
| Electronic state of the defect | $^2B_{2g}$ | $^4B_{1g}$ | $^4B_1$ | $^6A_{1g}$ |
| Total energy (in atomic units) | $-8982.11453$ | $-8982.13950$ | $-8982.16547$ | $-8982.15906$ |
| Energy loss (eV) | 1.386 | 0.706 | 0 | 0.174 |

used for defects with substitutional Mn impurity in the B position. This cluster was described in detail in [19]. The electronic problem was solved within the density-functional theory with the B3LYP hybrid functional [22–24] using the spin-unrestricted MO LCAO SCF method from the quantum-chemical GAUSSIAN 03 program package [25]. The calculation details (choice of atomic bases, etc.) were reported in [8, 19]. The spin–orbit interaction was disregarded.

Mn ATOM IN THE B POSITION IN SrTiO$_3$

The manganese atom can occupy the B position in SrTiO$_3$, substituting Ti and being completely octahedrally coordinated by oxygen atoms. In this case, the defect can be in either neutral (at least in nominally pure material) or charged states, for example, in the presence of distant donor centers or photoactivated carriers. Here we consider three charged states of the defect: $Z_d = 0$, $-1$, $-2$ (in atomic charge units $|e|$).

Due to the variable valence, Mn$_n$ allows for defects of different types, with the competition of several electronic defect configurations corresponding to the same $Z_d$ value. The following possible types of defects were considered in [8]: (1) Mn$^{4+}$, (2) Mn$^{3+} + p$, and (3) Mn$^{2+} + p$ for $Z_d = 0$; (4) Mn$^{5+}$ and (5) Mn$^{2+} + p$ for $Z_d = -1$; and (6) Mn$^{2+}$ for $Z_d = -2$. Here, $p$ denotes a hole (missing electron) localized on ligands (six neighboring oxygen atoms). The results of preliminary calculations for some of these configurations were also reported in [8]. This consideration is incomplete. It is generally necessary to consider a complete set of possible spin states of the defect which are allowed at these $Z_d$ values. As a result, a richer set of defect types arises [9]. In this study we performed a complete analysis of this situation, taking into account both the charge state and the multiplet spin structure of the defect. The calculation results are listed in Tables 1 and 2.

The state with the point symmetry $O_h$ and spin multiplicity $2S + 1 = 4$ [8, 9] is ground for the neutral defect. The spin density (which corresponds to the density of unpaired-spin electrons; i.e., electrons from unoccupied shells) is concentrated mainly at the Mn atom and amounts to 2.82, a value corresponding to $14.2$ eV Å$^{-2}$. The low-spin state of the Mn$^{4+}$ ion, as well as the Mn$^{3+} + p$ and Mn$^{3+} + 2p$ polaron states, have much higher energies.

For the singly charged defect ($Z_d = -1$), the ground state has the point symmetry $D_{4h}$ and spin multiplicity $2S + 1 = 5$ [9]. The indices $e$ and $s$ in the parentheses near the designation of the point symmetry group indicate, respectively, tensile and compression strains of oxygen octahedron. The spin density is mainly concentrated at the Mn atom and is equal to 3.71, a value corresponding to the state with a spin of 2, i.e., the...