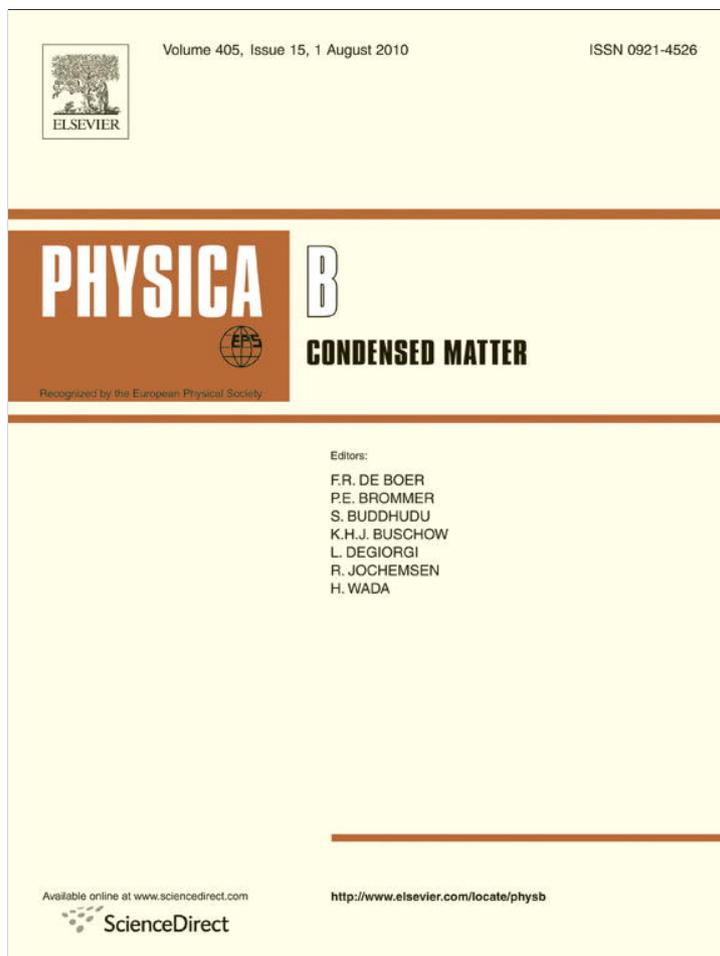


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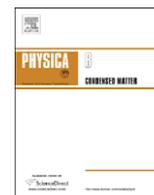


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Ab initio calculations of Nb doped SrTiO₃

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ABSTRACT

We present and discuss the results of the large scale Hartree–Fock calculations of Nb impurities substituting for Ti ions in SrTiO₃ using *ab initio* computer code CRYSTAL and several supercells containing up to 135 atoms. The local structure optimisation, the electronic charge redistribution, chemical bond covalence and the band-structure changes induced by the defect are analysed. According to the results of our calculations, Nb is a shallow donor; six nearest O ions are slightly displaced outwards from the Nb ion. The calculated bond population between nearest Ti and O ions (64 me) is much larger than that between Nb and O ions (8 me), since Nb impurity is more ionic than the host Ti.

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1. Introduction

Strontium titanate (SrTiO₃) is a prototype of a wide class of ABO₃-type perovskites. At room temperature it is a centrosymmetric paraelectric material, and reveals an anti-ferrodistortive phase transition at 105 K. At low temperatures it reveals a very large dielectric constant $\sim 10^4$ and approaches a ferroelectric phase transition but still remains incipient ferroelectric down to the lowest temperature measured. It was a long thought to be a wholly artificial material, until 1982 when its natural counterpart was discovered in Siberia and named *tausonite*. Tausonite remains an extremely rare mineral in nature, occurring as very tiny crystals. Its most important applications have been in its synthesized form wherein it is occasionally encountered as a diamond simulator, in precision optics, in varistors, and in advanced ceramics. SrTiO₃ is promising for many device applications because of its unique physical properties, in both bulk and thin-film forms. SrTiO₃ is among the best studied and most important perovskite titanates, as it is widely used as a dielectric material and as a substrate for growth of thin films or superlattices of other functional perovskite or related (e.g. high T_c) materials.

Nb-doped SrTiO₃ is also important for several high tech applications including anodes of solid oxide fuel cells [1] and non-volatile resistive switching memories [2]. Donor-doped SrTiO₃ ceramics have found applications also in sensors, varistors,

grain boundary layer capacitors and catalysts. For these reasons, a detailed understanding of the bulk and surface structure and electronic properties of Nb doped SrTiO₃ is of primary importance. Considering high technological importance of Nb doped SrTiO₃, it is not surprising that during the last years it has been the subject of many experimental studies [3–6], but better theoretical understanding is still necessary. The existing *ab initio* calculations were performed using DFT method combined with the plane wave basis set (CASTEP computer code) [7], full-potential linearized augmented plane waves (FLAPW) [8] and linear muffin-tin orbital approach (LMTO-ASA) [9]. The common disadvantage of the DFT method is considerable underestimate of the band gap of solids, typically 1.5–2 eV for SrTiO₃ instead of the experimental value of 3.3 eV. Due to this fact in most DFT calculations energy levels of donors fall erroneously into the conduction band. The second DFT problem is lack of analysis of effective atomic charges and charge redistribution caused by defects. Lastly, in most of these calculations rather small supercells were used, which do not eliminate artificial interaction of periodically distributed Nb ions. In this paper, we present and discuss the results of the Hartree–Fock (HF) calculations, which typically overestimate the band gap. In Section 2 the method is discussed, whereas the main results are presented in Section 3.

2. Computational method

To perform the *ab initio* HF calculations, we used the CRYSTAL-03 computer code [10]. This code employs the Gaussian-type functions (GTF) localized at atoms as the basis for the expansion of the crystalline orbitals. In order to employ the linear

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combination of atomic orbitals (LCAO)–GTF method, it is desirable to have optimised basis sets (BS) for the SrTiO₃ perovskite. Such optimisation for several perovskites was developed and discussed in Ref. [11] and successfully applied to SrTiO₃, BaTiO₃, PbTiO₃, CaTiO₃ and BaZrO₃ (0 0 1) and (0 1 1) surface structure calculations [12–15]. In this paper, we used this SrTiO₃ basis whereas for the Nb impurity we used the basis set from Ref. [16]. The Hay–Wadt small-core effective core pseudopotentials (ECP) were adopted for Sr and Ti atoms [17]. The “small-core” ECPs replace only the inner core orbitals, but orbitals for both valence and subvalence are calculated self-consistently. Light O atoms were treated with the all-electron BS as described in detail in Ref. [11].

The reciprocal space integration was performed by sampling the Brillouin zone with the Pack–Monkhorst mesh [18]. To achieve high accuracy, large enough tolerances of 7, 8, 7, 7 and 14 were chosen for the Coulomb overlap, Coulomb penetration, exchange overlap, first exchange pseudo-overlap and second exchange pseudo-overlap, respectively [10]. We used the experimental SrTiO₃ lattice constant (3.89 Å) extrapolated to 0 K temperature [19] and 135 atom supercells (5-atom unit cell expanded by $3 \times 3 \times 3$ along the translation vectors) where one Ti ion was replaced by the Nb ion. This corresponds to the defect concentration of 3.7%. All atoms in the supercell were allowed to relax to the minimum of the total energy. The effective atomic charges and chemical bond populations were calculated using the standard quantum chemical Mulliken population analysis.

3. Main results

The calculated average Sr charges in the supercell are 1.92e, very close to the formal charge of +2e. This is in contrast with Ti ions (2.77e) and O ions (−1.57e), which indicates considerable covalency of the chemical bonding (see below). For a single Nb ion, which replaces the Ti ion, we found the effective charge of 3.13e (instead of a formal charge +5e), i.e. by $\sim 0.4e$ larger than that of a host Ti ion. This additional charge is donated to surrounding O ions which become more negative.

The atomic structure optimisation shows the symmetrical and small (0.05 Å) outward displacement of six nearest O atoms from the Nb impurity (Fig. 1). The calculated bond populations between the nearest Ti and O ions indicate considerable covalency effect (see Table 1). In contrast, the bond population between the nearest Nb and O ions turns out to be much smaller, 8 vs. 64 me for the Ti–O bond. This results from the above discussed more

ionic charges of Nb and nearest O as compared to Ti and nearest O ions. The formal bond populations calculated between nearest Sr and O atoms are negative which indicates the absence of chemical interaction of these ions.

The calculated HF optical band gap is quite an overestimate, 12.5 eV. The Nb impurity band is located here 1.13 eV below the conduction band (CB) bottom. If we scale the band gap down to the experimental value, the Nb state would be located ca. 0.25 eV below the CB bottom, which means that this is a shallow donor.

Table 1

Calculated Mulliken bond populations P (me) between different atoms in Nb doped SrTiO₃ crystal using $3 \times 3 \times 3$ and $2 \times 2 \times 2$ (data in parentheses) extended supercells containing 135 and 40 atoms, respectively.

Atom A	Atom B	P (me)	R (Å)
Nb	O	8 (2)	1.995
Ti	O	64 (64)	1.945
Sr	O	−22 (−24)	2.751
Sr	Ti	0 (0)	3.369
Sr	Nb	0 (0)	3.369

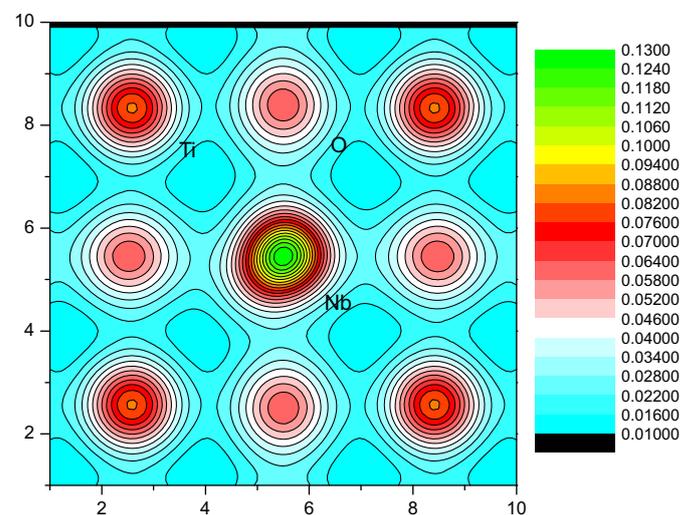


Fig. 2. Charge density map of Nb doped SrTiO₃ bulk from (0 0 1) side view calculated using $2 \times 2 \times 2$ extended SrTiO₃ supercell containing 40 atoms.

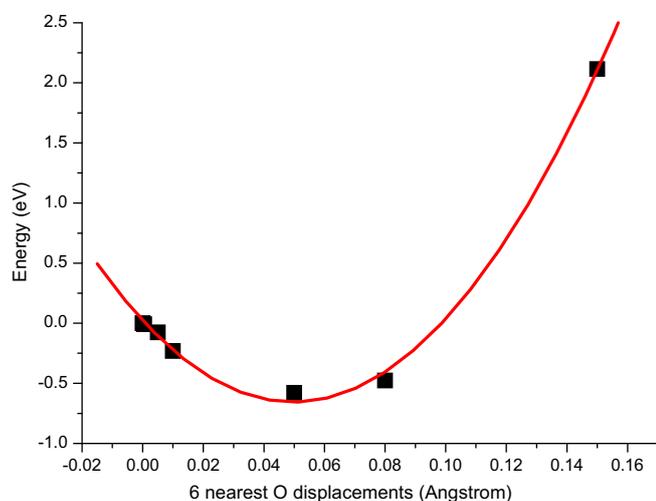


Fig. 1. Calculated relaxation energy around the Nb impurity in SrTiO₃ crystal.

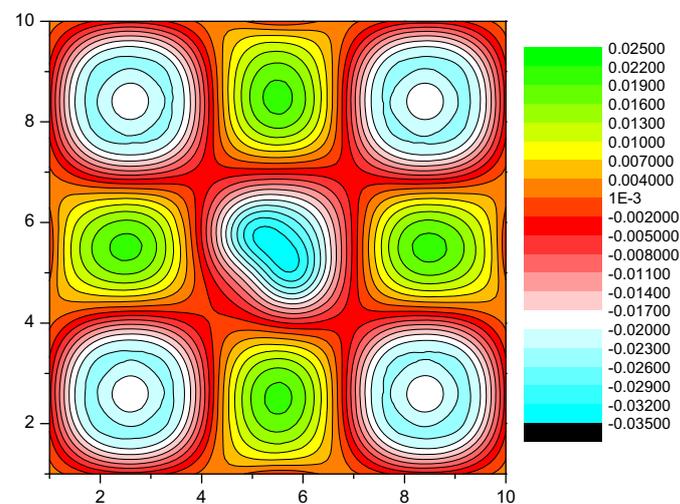


Fig. 3. Difference charge density map of Nb doped SrTiO₃ bulk from (0 0 1) side view calculated using $2 \times 2 \times 2$ extended SrTiO₃ supercell containing 40 atoms.

In order to analyze the effect of an interaction between periodically distributed Nb impurities, we performed similar calculations using the $2 \times 2 \times 2$ extended supercell containing 40 atoms. In this case, Nb impurity replaces each 8th Ti atom, and the Nb doping level increases to 12.5%. The main effect is that Nb effective charge is decreased (by 0.05e), as well as the bond populations between Nb and O ions (by 75%).

Fig. 2 shows the electronic charge density map of Nb doped SrTiO₃ bulk (the (0 0 1) plane). This confirms the population analysis about the covalent chemical bonding and larger effective charge of Nb ion compared to the host Ti ion. The difference charge density map in Fig. 3 is plotted for the same system (the superposition of neutral atom electron densities minus the self-consistent density for a crystal). One can see that the central ion (Nb) has the largest positive charge, Ti ions are less charged and O ions are negatively charged.

4. Conclusions

The *ab initio* HF calculations demonstrate that Nb ions substituting for host Ti ions in SrTiO₃ are shallow donors. Their incorporation results only in a small outward relaxation of nearest O ions. Due to larger Nb ion effective charge as compared to Ti, negligible chemical bonding between Nb and nearest O ions occurs (in contrast to the Ti–O bonding). It is useful to compare these results with other impurities on the Ti site. Recent studies using the same CRYSTAL computer code for the Fe impurity in the SrTiO₃ bulk [20] and on the surface [21] show that this is an acceptor. The calculated magnitude of the Jahn–Teller effect is in good agreement with the EXAFS experimental data [22]. This demonstrates that the first-principle calculations are a reliable tool for studying the defects in perovskite materials.

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